Dimitrios A. Giannakoudakis Teresa J. Bandosz

Detoxification of Chemical Warfare Agents

From WWI to Multifunctional Nanocomposite Approaches



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Contents

Che	mical Warfare Agents (CWAs)	1
1.1	The History of Chemical Warfare Agents	1
1.2	International Agreements Against CWAs	2
1.3	Classification of Chemical Warfare Agents	3
Refe	erences	3
Woi	d War I: Militarization of Chemistry	5
2.1	The Chronicle of the Vast Scale Usage of CWAs:	
	The Road to Mustard Gas	5
2.2	Casualties and Fatalities of WWI	9
2.3	First Protection Attempts: Pads, Helmets, and Gas Masks	14
	2.3.1 The Germans	14
	2.3.2 The British	16
	2.3.3 The French	18
	2.3.4 The Italians	20
	2.3.5 The Russians	21
	2.3.6 The Americans	21
Refe	erences	25
Mus	stard Gas: The King of CWAs	27
3.1	Mustard Gas	27
3.2	Mustard Gas Deployment Post the WWI	28
3.3	Proposed Decomposition Pathways of HD	29
3.4	The Surrogate of Mustard Gas	30
	3.4.1 Detoxification Pathways of the Mustard Gas	
	Surrogate, CEES	30
Refe	erences	31
	Che 1.1 1.2 1.3 Refe Won 2.1 2.2 2.3 Refe Mus 3.1 3.2 3.3 3.4 Refe	Chemical Warfare Agents (CWAs) 1.1 The History of Chemical Warfare Agents 1.2 International Agreements Against CWAs 1.3 Classification of Chemical Warfare Agents References

4	Cur	rent Pr	rotection Against CWAs	33
	4.1	Whetl	erites: The Improved Military Activated Carbon	33
	4.2	Resear	rch on New Adsorption/Detoxification Materials	34
	Refe	erences		36
5	New	Appro	paches in the Detoxification of CWAs	37
	5.1	Zinc (Hydr)Oxide-Based Multifunctional Nanocomposites	37
		5.1.1	One-Pot Wet Precipitation of Zinc (Hydr)Oxide	37
		5.1.2	$Zn(OH)_2$ Versus ZnO: The Key Role of the Hydroxyl	
			Groups	43
		5.1.3	Effect of GO Phase in Zn(OH) ₂ /GO Composites	
			on the Extent of Photocatalytic Reactive Adsorption	57
		5.1.4	AuNPs and AgNPs Embedded in Nanostructured	
			Composites of Zinc (Hydr)Oxide/GO	76
	5.2	Zircon	nium (Hydr)Oxide-Based Multifunctional	
		Nanoc	composites	90
		5.2.1	Effect of GO Phase in ZR(OH) ₄ /GO Composites	
			on the Extent of Catalytic Reactive Adsorption	90
		5.2.2	AgNPs Embedded in Zirconium Hydroxide/GO	
			Composites	107
	Refe	erences		118
6	Path	n Towa	rds Future Research	125
	6.1	Oxidiz	zed Graphitic Carbon Nitride Nanospheres	
		as a N	Iew Composite Component	125
		6.1.1	Graphitic Carbon Nitride	125
		6.1.2	Oxidized Graphitic Carbon Nitride Nanospheres	126
		6.1.3	Graphitic Carbon Nitride Nanospheres as CEES	
			Detoxification Media	128
		6.1.4	MOFGCNox Composites as Detoxification Media	129
	6.2	Mixed	l (Hydr)Oxides	131
	6.3	Reacti	ve and Smart Textiles	134
		6.3.1	Porous Carbon Fabrics	135
		6.3.2	Cotton Fabrics with Deposited Ferrihydrite	137
		6.3.3	Smart Textiles	138
	Refe	erences		141

Chapter 1 Chemical Warfare Agents (CWAs)

1.1 The History of Chemical Warfare Agents

The extended usage of chemicals as weapons dates since classical times, when lighting of bonfires, irritant smokes, and several compositions of pitch, petroleum, and sulfur (Greek fire) delivered a serious advancement for a mass troop elimination. Even ancient history indicates the use of toxic chemicals to defeat enemies. Homer mentioned in his epics (the Iliad and the Odyssey) the use of poisons arrows in Trojan War (around 1200 BCE) [1]. Poisonous heart-toxic extracts from hellebore plants were used by Athenian forces in 600 BCE to taint the water supply during the besiege of Kirrha against Spartans [1]. Around 120 years later, Peloponnesian military used sulfur fumes to trigger off the evacuation of the city of Plataea [2]. In the middle of the eighteenth century (1845), the French troops cornered more than 1000 people into a cave during the conquest of Algeria and executed them using smoke.

The First World War (WWI) brought out a prolonged vast scale usage of chemical warfare agents (CWAs), which can be considered as the saddest reality in the modern history. More than 50 different CWAs were deployed, while above 3000 compounds were investigated as potential weapons [3]. Even though it is believed that the German army was the first one to use poison gases, that race was in fact opened by the French army that first deployed tear gas grenades in 1914 [4]. Since that time, the active involvement of chemistry in the war has begun. Many compounds were afterward tested in the battlefields as CWAs. Most CWA-related injuries and deaths during WWI were linked to three toxic compounds: chlorine, phosgene, and sulfur mustard. At the beginning of WWI, the German military established research centers to develop chemicals as weapons of mass destruction. Many recognized scientists were involved in the synthesis of CWAs. That list includes Nobel Prize laureates such as Max Planck (Physic, 1918), Fritz Haber (Chemistry, 1918), Wulther Nernst (Chemistry, 1920), James Franck (Physic, 1925), Gustac Hertz (Physic, 1925), and Otto Hahn (Chemistry, 1944). The Allied forces did not stay behind, and they also started an extensive research on the development of CWAs, as well as on protection medias,

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basically on gas masks. As Daniel Charles pointed out in his book, "A new era had dawned in the uses of chemistry" [5].

1.2 International Agreements Against CWAs

The first international agreement that prohibited the use of poison bullets was signed by France and German in Strasbourg (1675) [6]. In 1874, the Brussels Convention on the "Law and Customs of War" banned the employment of poison or poisoned weapons, and the use of arms, projectiles, or materials to cause unnecessary suffering. Another agreement was signed during an international peace conference in Hague (1899), which prohibited the deployment of projectiles filled with poisonous gas. These agreements proved to be worthless, since through the World War I, toxic gases were utilized on a massive level, leading to more than one million of casualties and more than one hundred thousand fatalities. International efforts to forbid the usage of chemical weapons (CWs) resulted in a renewed global commitment, the 1925 Geneva Protocol.

Although the deployment of asphyxiating, poisonous or other gases, and bacteriological methods of warfare had been banned, this commitment did not prohibit the development, production, or possession of CWAs. It is believed that the Geneva Protocol played a crucial role in the absence of CWAs during the World War II (WWII), fortunately. It happened in spite of the fact that almost all involved countries had stockpiled numerous toxic compounds, ready to be used. It is believed that Hitler, as a victim of the first mustard gas deployment during WWI, was against the usage of CWAs in battlefields. Nevertheless, it has to be mentioned here that German SS massacred millions in the extermination camps using the toxic pesticide, Zyklon B (silica adsorbed cyanide).

The latest agreement was signed in 1993 at the Chemical Weapons Convention (CWC). This international treaty outlaws the production, stockpiling, and deployment of chemical weapons. The convention's full title is "*Convention on the Prohibition of the Development, Production, Stockpiling and Use of Chemical Weapons and on their Destruction.*" An independent Organization for the Prohibition of Chemical Weapons (OPCW), established in Hague, is responsible for the enforcement of this agreement. OPCW Mission states: "The mission of the OPCW is to implement the provisions of the Chemical Weapons Convention (CWC) in order to achieve the OPCW's vision of a world free of chemical weapons and the threat of their use, with the cooperation of chemistry for peaceful purposes. In order this vision to be accomplished, our ultimate aim is to contribute to international security and stability, to general and complete disarmament, and to global economic development" [7].

Today, 192 OPCW members represent about 98% of the global population, landmass, and worldwide chemical industry [7]. According to OPCW, 92% of the 72,525 metric tones stockpiled CWAs have been verified to be destroyed by June 2016 [7]. In recognition of this effort to eliminate CWAs, OPCW was awarded the Nobel Peace Prize in 2013.

1.3 Classification of Chemical Warfare Agents

Chemical Warfare Agents (CWAs) can be considered as the most brutal weapons among all the weapons of mass destruction. According to OPCW: "The term chemical weapon may also be applied to any toxic chemical or its precursor that can cause death, injury, temporary incapacitation or sensory irritation through its chemical action. Munitions or other delivery devices designed to deliver chemical weapons, whether filled or unfilled, are also considered weapons themselves" [7].

CWAs can be classified in various ways. From a chemical structure viewpoint, the main categories are organosulfur, organofluorine, organophosphorus, and arsenical compounds. They can be also categorized based on their volatility. Phosgene, hydrogen cyanide, and chlorine are volatile agents, while sulfur mustard and most of the nerve agents are less volatile. The most common classification is in terms of the effects on humans [8]. Based on that, the categories of CWAs (and some examples of CWAs used during WWI) are as follows:

- Lachrymatory: tear gases such as benzyl bromide
- Vesicants/blistering agents: mustard gas, lewisite
- Blood/asphyxiant agents: hydrogen cyanide, cyanogen chloride, many arsines
- Choking/pulmonary agents: chlorine, chloropicrin, phosgene
- Nerve agents
- Psychomimetic agents
- Toxins

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Chapter 2 World War I: Militarization of Chemistry

2.1 The Chronicle of the Vast Scale Usage of CWAs: The Road to Mustard Gas

The opening act of the toxic gases deployment took place at the early months of WWI, when the French army fired tear gas grenades (filled with ethyl bromoacetate) against German soldiers (August 1914) [1]. These grenades were manufactured prior to the war and first deployed by French police in 1912, in order to crush riots in Paris. Following the recommendation of Walter Nernst (Nobel Prize in Chemistry; 1920), the German forces filled shells with dianisidine chlorosulfonate powder, which was readily available due to its extensive use as an intermediate in the synthetic dye industry [2, 3]. Around 300 filled shells, called Ni-Schrapnell or N-J shells, were fired against the British army from the Germans at the capture of Neuve Chapelle in France on October 27, 1914, but without any effect except of a violent fit of sneezing. In December 1914, benzyl bromides were also tried [4]. These incidents of failure served to permanently change the course of war. A chemist, who participated in the war without any military rank, became inspired and dedicated himself to apply this novel aspect of chemistry in the battlefields. His name was Fritz Haber. He played a vital role in persuading the German generals to begin the development of toxic gases for a mass scale usage as a weapon and to use them in the actual battles.

Three months later, the German forces fired more than 18,000 "T-shells" containing liquefied tear gas, xylyl bromide, on the Eastern Front during the battle of Bolimów (January 31, 1915). All three isomers of xylyl bromide or methyl benzyl bromide (C_8H_9Br) are highly toxic and irritant. Due to the extreme low temperature in Bolimów, the liquid did not vaporize and the attack proved to be a complete failure. Similar unsuccessful attacks with improved tear gas mixtures were carried out against the French army in March 1915 at Nieuwpoort in Belgium. Due to the simplicity of the xylyl bromide production, it was widely used by Germans during the war as a component of the white cross mixture (Weisskreuz) in the artillery shells. Other chemical compounds were also applied in shells and grenades as tear gases, among them chloromethyl chloroformate and bromoacetone. For the mass production of these shells, specialized factories were built. The main drawbacks were the difficult and time-consuming production and transportation of those shells to the battlefields. The shell shortage in many occasions revealed the necessity of alternative ways of chemicals deployment to the battlefields.

Haber's suggestion to use gas from pressurized tanks as CWAs, instead of using them merely in the shells was approved by Germans generals in January 1915. His fast efforts led to around 5700 cylinders containing more than 340 tons of chlorine stocked by April 11 of that year [5]. The German army was waiting for a suitable speed and orientation of wind in order to launch a chlorine attack. On April 22, 1915, the first deployment of chlorine as weaponry gas became a reality at the second battle in Ypres. The consequences of a greenish-yellow chlorine cloud were more than 1100 dead and 7000 injured soldiers. The Allied troops fled in disorder, and the German infantry easily advanced and conquered the French trenches. This act rose the moral of the German troops, and Haber was promoted from a sergeant of the reserves to a captain.

Haber concluded that those toxic clouds were very effective since they not only led to asphyxiation, but also to a total depletion of the enemies' front lines. His confidence that chemistry could have an active involvement in the war as an effective weapon changed once for good the path of war. The British were the first from the Allied forces that tried to respond with a chemical gas attack on September 24th, 1915. Unfortunately, the first deployment of a mixture of smoke and chlorine gas from around 400 gas tanks, in the front line at Loos in France led to an unexpected effect, since the wind shifted and the gases were blown to an opposite direction, resulting in more British casualties than the German ones [1]. The use of pure chlorine was gradually abandoned, but it was widely used in mixtures with phosgene and chloropicrin [6]. The latter, also called trichloronitromethane, (CCl₃NO₂) was introduced as a chemical weapon by Russian forces in July 1916. The British used a mixture of chloropicrin with chlorine (30:70), called Yellow Star gas [4]. Chloropicrin is an eye irritant, which had the ability to penetrate earliest gas masks, forcing the soldiers to remove the masks. The development of filters from charcoal eliminated the chloropicrin effects.

A more lethal combination of chlorine with a 5% chocking agent, phosgene, was widely used by the German army against the Russian army of the Eastern front and against the French troops on the Western front by the end of May 1915. That mixture was also used on June 12 and July 6, 1915, in Bolimów and in October against the French army. The casualties of the latter usage were huge, since the French soldiers were totally unprotected against phosgene. Phosgene or carbonyl dichloride (COCl₂) was synthesized by John Davy in 1812, and it is considered as one of the most dangerous existing CWAs. He named it from the combination of the Greek words "*phos*" (meaning light) and "*genesis*" (meaning birth), since sunlight exposure was mandatory for the synthesis from a mixture of chlorine and carbon monoxide [7]. The use of poison gas mixtures of chlorine with higher amount of phosgene (25%) was successfully introduced in the battlefields by the

German army, six days before Christmas of 1915. It led to 120 death and more than 1000 injured British soldiers [5]. Even though the amount of the gases deployed at that battle was significantly greater than the one against the French in October, the casualties were lower, since the British were equipped with gas masks.

Phosgene was by far the deadliest CWAs used during WWI. It is 10 times more toxic than chlorine, volatile above 8 °C, and its vapor density is almost four times higher than that of air. From the estimated 100,000 recorded fatalities from poisonous gases, 85% were attributed to phosgene. Most of the times, it was used with chlorine in order to improve the spread of the denser phosgene. The major advantage compared to chlorine was the difficulty to be sensed by the victims since its vapors are colorless and have the smell of freshly cut grass. The first symptoms such as a burning sensation of a throat, watery eyes, and nausea appear gradually after 15 min. Survival rates are very low, due to the aggressive disruption of the blood-air barrier in the lungs [8]. After 24 hours, the formed tinged liquid in the lungs or the low blood pressure results in death. In addition, contact with the skin leads to blisters.

Carbonyl dichloride is an important chemical for the industrial manufacturing of dyes, pigments, plastics, and pesticides. It is used up today. The largest German industrial companies, such as BASF and Bayer, were producing phosgene prior to WWI, but its application as CWA in December 1915 is attributed to Fritz Haber [9], although the first introduction of phosgene to the battlefields in a small scale was by the French army some months prior. The French Nobel laureate Victor Grignard synthesized it [10].

Both sides developed distinct masks in order to neutralize phosgene, a few months after its first deployment. As a response to the gas masks, the German army developed another CWA, trichloromethyl chloroformate, known as diphosgene (DP, $CICO_2CCl_3$), that is related to phosgene, with comparable toxicity and with the ability to pass through or to destroy the filters used in the first gas masks. The first documented use of diphosgene was in artillery shells on the Western Front in May 1916 [5].

The French army replied to the phosgene by using the simplest unsaturated aldehyde, propenal, or acrolein, as a filler for artillery gas shells and gas grenades. Acrolein had a code name *Papite*, and its first deployment was in January, 1916. It is a colorless liquid at room temperature with a characteristic intense acrid smell. The characteristic smell of the burnt fat/oil is due to the formation of acrolein during the decomposition of glycerol. Even though this unsaturated aldehyde acts simultaneously as tear gas and, more importantly, as an irritant agent for the skin, nasal passages, and lungs at high concentrations, it was proven to be not effective in the battlefields because of its chemical instability.

The next used CWA, Mustard gas (HD), made its debut in a gas cloud attack on Allied troops near Ypres on 12th of July, 1917. It was the most effective CWA of WWI, since it was broadly used in huge quantities to harass and disable the defense trenches before the attacks. The consequences of nearly 6000 cylinders used in the first deployment were more than 2200 casualties. Initially, Germans planned to use this gas only as a paralyzing and blister agent. However, they realized soon that in

sufficient doses, it could be lethal to the enemy soldiers. The fatally exposed victims confronted extreme pain and sometimes were afflicted for up to five weeks before they finally passed away. The first aid camps were fully occupied for months with Mustard gas exposed soldiers and civilians. More than a million tons of HD, placed in artillery shells, were launched in the following month at the battle at Ypres. Besides, Mustard gas was deployed by various means, even by spraying from warplanes. This effective CWA elevated the moral of the German forces. The shells that contained Mustard gas were marked yellow, compared to the green-marked shells contained chlorine and phosgene. The yellow assignment came as a result of the yellow-brown color of impure gas clouds. Although not as lethal as other used CWAs, the devastating consequences of the extremely painful blisters, the internal and external bleeding of the victims, the difficulties to manufacture effective protection media, and the contamination of the soil for a long period of time shocked the world and attracted the worldwide attention. Mustard gas was established as the king of the battle gases and became the most popular CWA. The most widely deployed CWAs by the German forces are collected in Fig. 2.1.



Fig. 2.1 Major chemical warfare agents deployed by the German army during the World War I (in a chronological order)

Another lethal warfare agent was developed for the US army by Captain Winford Lee Lewis from the Chemical Warfare Service (CWS) laboratory in Washington D.C. It was formed by the reaction of acetylene with arsenic tetrachloride. Its synthesis was first reported in the PhD Thesis of a priest-chemist Father Julius Arthur Nieuwland in 1904. That organoarsenic compound, 2-chloroethenylarsonous dichloride (ClCH=CHAsCl₂), was referred to as Lewisite. It is a blister (vesicant) and lung irritant agent that acts similarly to Mustard gas. It has the ability to penetrate the normal soldiers' clothing, and even to go through rubber or latex textiles. In its pure form, it is odorless and colorless. This new toxic compound was thought to be effective during WWI, since it was unknown to the Central Powers. A special factory was constructed in the USA (Willoughby) for a massive production of Lewisite, which started few days before WWI ended. Fortunately, this compound was never deployed, since the war ended prior to its arrival to Europe.

The chemical compounds most widely deployed as CWAs during WWI in a chronological order, along with their military code names and their effects on a human body are listed in Table 2.1. The details are collected from various sources [6, 11-16].

2.2 Casualties and Fatalities of WWI

The Great War (WWI) and WWII are the deadliest conflicts in the modern history. There are various estimations of casualties and deaths caused by CWAs, and it is impossible to accurately calculate the victims. The main reason is the lack of precise records, since not all the casualties were recorded, or they were initially recorded in other general categories such as "prisoners and missing people". Moreover, not all countries released official records. Nevertheless, the existing estimations from various sources are similar. Based on the official reports from Robert Schuman European Centre (CERS) and the US War Department in 1924, the total number of the recruited soldiers/mobilized forces from both sides was higher than 64 million. The casualties (deaths, wounded, prisoned, and missing) reached more than 37 million (58% of the mobilized personnel). Details of the casualties per country can be seen in Fig. 2.2. The casualties of Russian army were the highest, followed by those of the two main empires of the Central Powers, Germany, and Austria-Hungary.

The total number of the casualties during the WWI reached almost 45 million, which includes around 7 million of non-mobilized civilians. The Allies powers lost 25.7 million and the Central Power—18.5 million. The percentages of the total casualties by country are collected in Fig. 2.3.

A detailed analysis of the casualties is presented in Table 2.2. In this Table, the percentage of the total casualties per population of the country is also included. Sadly, these numbers reached 17.4% for Serbia, 16.3% for France, 14.7% for Turkey, 14.6% for Austria-Hungary, and 11.7% for the German Empire. Even though Russia suffered from the highest number of casualties, the percentage of the

Table	2.1 Chronicle of the most widely used chen	nical comp	ounds as	s CWAs d	uring WW	I, their militaı	y code names, and th	eir effects on a human body
Year	Agent	First use	р	Used	Military o	code name		Effect
		Month	By	by	British/ US	French	German	
1914	Ethyl bromoacetate	Aug.	Allies	Both	EBA	I	(White cross)	Lachrymatory
	Dianiside salts	Oct	Germ.	Germ.	I	I	1	Irritant
	Chloroacetone	Nov.	Allies	Both	I	Tonite	A-Stoff (White cross)	Lachrymatory, irritant
	Benzyl bromide	Dec.	Germ.	Both	1	Cyclite	T-Stoff	Lachrymatory
1915	Xylyl bromide	Jan.	Germ.	Both	I	1	T-Stoff	Lachrymatory
							(White cross)	
	Benzyl iodide	Mar.	Allies	Allies	Ι	Fraisinite	I	Irritant, lachrymatory
	Chlorine	Apr.	Germ.	Both	I	Bertholite	Chlor	Lung irritant, corrosive
	Ethyl chlorosulfonate	Apr.	Allies	Allies	I	Sulvinite	I	Lachrymatory, irritant
	Bromine	May	Germ.	Germ.	Ι	I	Brom	Irritant
	Phosgene (carbonyl dichloride)	May	Germ.	Both	CG	Collongite	(Green cross)	Irritant, toxic, corosive
	Methyl chlorosulfonate	June	Germ.	Both	I	Villantite	C-Stoff	Lachrymatory, irritant
	Bromoacetone	June	Germ.	Both	BA	Martonite	B-Stoff (White cross)	Lachrymatory, irritant
	Dimethyl sulfate	Aug.	Germ.	Germ.	1	1	D-Stoff	Irritant
	Perchloromethyl mercaptan	Sept.	Allies	Allies	1	Clairsite	1	Irritant
	Ethyl iodoacetate	Dec.	Allies	Allies	SK	I	1	Lachrymatory, toxic
1916	Acrolein (propenal)	Jan.	Allies	Allies	I	Papite	1	Lachrymatory, toxic
	Disphogene (trichloromethyl chloroformate)	May	Germ.	Both	DP	Surpalite	Perstoff (Green cross)	Irritant, vesicant
	Hydrogen cyanide	July	Allies	Allies	AC	Forestite	1	Toxic, asphyxiate
								(continued)

10

(continued)	
2.1	
Table 2	

Year	Agent	First use	p	Used	Military .	code name		Effect
		Month	By	by	British/ US	French	German	
	Chloropicrin (Trichloronitromethane)	July	Allies	Both	PS	Aquinite	Klop (Green cross)	Irritant, toxic, lachrymatory
	Cyanogen bromide	July	allies	Both		Campilite	E-Stoff	Irritant, toxic, asphyxiate
	Cyanogen chloride	July	Allies	Allies	CK	Mauguinite	1	Irritant, toxic, asphyxiate
1917	Diphenylchloroarsine	July	Germ.	Both	DA	I	Clark I (Blue	Vomiting agents
							cross)	
	Mustard gas (Bis(2-chloroethyl) sulfide)	July	Germ.	Both	HD/	Yperite	Lost (Yellow	Vesicant, lung irritant
					HS		cross)	
	Phenyldichloroarsine	Sept.	Germ.	Germ.	Ι	I	I	Vomiting agents



Fig. 2.2 Casualties of the mobilized personnel by country As reported by the US War Department in February 1924. US casualties as amended by the Statistical Services Center, Office of the Secretary of Defense, Nov. 7, 1957



Fig. 2.3 Percentages of the total casualties of the main countries involved in WWI

Table 2.2 Numb	ers of the cas	ualties of W	WI (base	d on the rep	orts from th	he US War	Department	and the Encyclopedia	a Britannica)	
Country	Total casualties (thousands)	Total soldiers casualties	Killed and died	Wounded	Prisoners and missing	Civilian deaths	Total mobilized forces	Soldiers casualties per mobilized forces (%)	Population (millions)	Percentage of total casualties per population
Allied powers										
Russia	10,650	9,150	1,700	4,950	2,500	1,500	12,000	76.3	175.1	6.1
France	6,460	6,160	1,357	4,266	537	300	8,410	73.2	39.6	16.3
British Empire	3,301	3,190	908	2,090	191	111	8,904	35.8	45.4	7.3
Italy	2,786	2,197	650	947	600	589	5,615	39.1	35.6	7.8
Romania	965	535	335	120	80	430	750	71.3	7.5	12.9
Serbia	781	331	45	133	153	450	707	46.8	4.5	17.4
United States	326	323	116	204	5	1	4,355	7.4	92.0	0.4
Greece	177	27	5	21	1	150	230	11.7	4.8	3.7
Belgium	155	93	14	45	35	62	267	34.8	7.4	2.1
Portugal	115	33	7	14	12	82	100	33.0	6.0	1.9
Allied Pow. Total	25,716	22,039	5,130	12,790	4,114	3,593	41,338	53.3	417.9	6.2
Central powers										
German Empire	7,569	7,143	1,774	4,216	1,153	426	11,000	64.9	64.9	11.7
Austria-Hungary	7,487	7,020	1,200	3,620	2,200	467	7,800	90.0	51.4	14.6
Turkey	3,125	975	325	400	250	2,150	2,850	34.2	21.3	14.7
Bulgaria	367	266	87	152	27	100	1,200	22.2	5.5	6.7
Central Pow. Total	18,547	15,404	3,386	8,388	3,630	3,143	22,850	67.4	143.1	13.0
Grand total	44,264	37,443	8,516	21,178	7,744	6,736	64,188	58.0	561	7.9
As reported by the https://www.britam	US War Depai	rtment in Febi /World-War-J	ruary 1924 I/Killed-w	 US casualti ounded-and-i 	ies as amendo missing	ed by the St	atistical Servio	ces Center, Office of th	e Secretary of	Defense, Nov. 7, 1957.



Fig. 2.4 Percentages of soldier casualties by country, out of the around 1,131,000 total recorded gas casualties (a), and the deaths per country (b) caused by CWAs [17]

total casualties per population was only 6.1%. The lowest percent of the total casualties per population was for the USA (0.4%), since it entered the war only some months before the Armistice (11 November 1918).

From the existing data, the total casualties directly linked to CWAs exceeded one million (1,131,000), while the fatalities reached almost one hundred thousand (Fig. 2.4). Russia suffered the highest number of casualties and deaths, since the soldiers were totally unprepared during the first gas attacks. Phosgene was responsible for the most deaths, while Mustard gas contributed dramatically to the increase in the number of casualties. Only 5% of those exposed to mustard gas were killed.

As the war was progressing, the number of the casualties decreased gradually. It was owing to the gas masks development. Fritz Haber was in favor of CWAs until his death. In 1919, he stated: "Chemical warfare is certainly no more horrible than flying pieces of steel; on the other hand, the mortality from gas injuries is smaller" [18]. And from the casualties' point of view, he was correct. Less than 1% of the total fatalities during WWI were from poisonous gases [19].

2.3 First Protection Attempts: Pads, Helmets, and Gas Masks

2.3.1 The Germans

The German Empire had many advantages at the beginning of WWI. Besides the foundation of special research groups focused on the toxic gases development, they had access to activated charcoal with an extremely high surface area, in addition to the porous mineral, diatomite. The latter is a soft, fine-grained, white siliceous sedimentary mineral, with an ultralow density (0.12–0.25 gcm⁻¹) and high porosity, also known as diatomaceous earth, kieselgur, or tripolite [20]. Diatomite consists of predominantly silica (>80%), alumina (2–4%), and iron oxide (0,5–2%)

[21], and it is chemically inert in various gases and liquids. Diatomite is formed by accumulation and compaction of diatoms, which are single-cell aquatic plants (algae) and one of the most common classes of phytoplankton. Diatoms' cell is surrounded/impregnated by a hydrated silicon dioxide wall. The distinctive property to adsorb and retain large amounts of liquids, even more than five times of its own mass, was the main reason for the establishment of this natural material as an industrial filtration medium. Ancient Greeks were the first to use diatomite for bricks and pottery. Germans used diatomite inside the canister of gas masks. It was impregnated with liquid detoxification solutions.

Charcoal is the product of the pyrolysis of various natural substances in the absence of oxygen. It is a lightweight and porous material predominantly consisting of carbon. Depending on the origin of its precursor, a charcoal surface can contain various chemical elements and functional groups. Numerous substances were explored as charcoal precursors during WWI. The chemical or thermal modifications led to materials of extraordinary adsorption properties—activated carbons. These properties are linked to a high surface area (over 1000 m²/g) and pore volume, which made activated carbons the most widely used materials in various environmental remediation applications [22]. Rafal Ostrejko was the first one to patent activation of charcoal, and he is considered as the father of activated carbon and its industrial applications. Ostrejko was born in 1893 near Jonava in Lithuania (part of the Russia Empire during WWI) from Polish nationality parents, and he studied chemistry in Latvia. His most worth to mention patents were the chemical activation with CaCl₂ (1900) and thermal activation by CO₂ or steam at high temperatures (1903) [22].

The combination of charcoal and diatomite was used as the first filler placed in a metal drum of gas masks referred to as Gummimaske. Diatomite impregnated with a potash solution was effective against chlorine, while activated charcoal—against various organic compounds. This filter had the code name "26/8", originating likely from the date of its establishment as the main canister. Starting in September 1915 and by the end of that year, almost all German soldiers at the front lines were equipped with gas masks. Professor of Chemistry at the University of Berlin and Director of the Kaiser Wilhelm Institute for Chemistry, Richard Willstätter, together with the chairman of Bayer Leverkusen Dyeworks, Carl Duisberg, established a procedure to produce granules of diatomite and activated charcoal [5]. Richard Willstätter was invited by Fritz Haber in 1915 to participate in the development of new toxic gases, but Willstätter agreed to be involved only in the development of new protection media. Willstätter was a Nobel laureate in chemistry in 1915, for his researches on plant pigments, especially chlorophyll [23].

The phosgene deployment by the Allied forces raised the need of an efficient filter for phosgene that would be based on the physical adsorption of organic gases/ vapors. Thus, the upgraded metal drum version, "11/11", had three layers. The outer layer was the same mixture as that used in the version 26/8. The middle layer consisted of charcoal granules for the adsorption of phosgene and other organic toxic gases, while the last layer was again diatomite, impregnated in this case with hexamine and potash. This version was applied in battlefields from April 1916. In

order to further increase the efficiency and to add protection against chloropicrin used by the British, an updated filter drum, with the code name 11-C-11, was introduced in June 1917. More charcoal was used in that filter. Another possible reason for its development was a potential usage of mustard gas. In the later "Lederschutzmaske" (Leather protection mask) model M1917, waterproof leather embedded in oil was used instead of rubber, with glass disk-shaped eyepieces. The M1917 model was introduced in August 1917. The metal filter canister was removable, but no intake or exhaust valves were used.

2.3.2 The British

The first vast scaled chlorine gas attack caught the Allies completely unprepared. Afterward, a great effort was made to manufacture protection masks. The first home-made attempt was the usage of cotton wool mouth pads, wetted with a neutralizing solution (urine or bicarbonate soda) [24]. The British named this respiratory Daily Mail. It was used at the chlorine attack on May 1st, 1915. Sadly, it was almost completely useless, because the wetted pads resulted in a completely airtight mass with difficulties in breathing. In an updated version, a pad of cotton waste has been used instead of cotton wool in order to avoid the breathing problems. This pad was soaked with a mixture if sodium hyposulfite, glycerin, sodium carbonate, and water, which can chemically neutralize chlorine, sulfur dioxide, and nitrous fumes. This mixture was established after the analysis of a respirator obtained from a German soldier-prisoner. Gauze was used to hold the pad while the ends were plainly knotted around the head. This updated version took the name Black Veiling Respirator, because black mourning gauze was used. Although the breathing problem was solved with the Black Veiling Respirator, it was difficult to get tied in rush and its effectiveness lasted only for about 5 min. In spite of these limitations, Black Veiling Respirator saved hundreds of lives during the chlorine attack of May 24, 1915, since almost all the British troops were equipped with one respirator by 20th May. Moreover, it provided the option to protect the eyes from tear gases by using a part of the veiling to cover the eyes.

The next attempt was inspired by witnessing a German soldier placing a bag over his head during a gas attack. This new mask was made by an impregnated fabric at the shape of a bag with a rectangular window to provide visibility and had no inlet or exhaust valve. It was easy to put on in rush, since the soldier had only to wear and place the bottom part of the mask into the uniform. It was known as the Hypo Helmet or the British Smoke Hood, since it was impregnated with hypo solution (sodium thiosulfate, sodium hyposulfate, and glycerin). The main disadvantage of this early model was that the rectangular celluloid window was very fragile. More than 2.5 million units of Hypo Helmet were used between May and September 1915, since it was able to efficiently protect against chlorine for three hours.

Hypo Helmet was displaced by the P Helmet in July 1915, due to the need of protection against phosgene and hydrogen cyanide (HCN). The letter "P" was from the protection against phosgene. This helmet consisted of two layers of cotton flannelette, to increase the corrosion protection of the single woolen layer. Sodium phenate was used for the protection against phosgene and HCN. The single celluloid window was replaced by two cyclic glass eyepieces. Carbon dioxide from breathing had a negative effect against hydrogen cyanide, and for that reason a valve was applied for the exhaled air. This type of mask went through numerous stages of development until it was succeeded by canister based gas masks, in 1916. P Helmet saved lives of numerous British soldiers at the biggest gas attack with the mixture of chloride and 25% phosgene on December 19, 1915. The helmets were later impregnated with a phenate-hexamine solution after Russia reported a high efficiency of hexamine or hexamethylenetetramine (C₆H₁₂N₄) for absorption of phosgene. This improved mask was called P. H. Helmet and it started to replace the P. H. Helmets in November 1916. In order to increase the protection against tear gases, rubber sponge goggles were placed inside the face piece in the middle of January 1916. This was the last model of the series "Helmet", known by the name P. H. G. Helmet. In spite of the severe limitations, such as an inefficiency in high toxic gas concentrations, poor visibility, vulnerability to the rain and the blisters at the neck, these masks became the most precious asset for soldiers, encouraging them to stay in the trenches and fight.

The next step in the gas mask development was the Large Box Respirator (LBR), designed by Edward Harrison, trying to overcome the above-mentioned disadvantages of the helmets. Moreover, there was always the fear that the Germans will use new toxic gases. The Allied forces initially had no knowledge on active charcoal, which was proven to be very efficient in its application in the Germans' canisters. First LBRs used a water flask, with three layers of neutralizing agents. The first layer consisted of potassium permanganate granules, the second—of small pumice pieces (soda lime) impregnated with sodium sulfate solution, while the third one—of charcoal. The filter-flask was connected to the mouth mask via a rubber tube. The fabric used in this mask had been soaked in hexamine-zinc solution and an exhaustion valve was installed. This complex system proved to be bulky to be used by the infantry, difficult for a massive production and very faulty. It was first introduced in February 1916 for officers and soldiers with special tasks who had stable and strategically crucial positions away from the frontlines.

The upgraded version of LBR was the Small Box Respirator (SBR). The filter system size of SBR was more compact and lighter than the previous one. These features enabled the use of those masks by the infantry. The lime-permanganate granules were deposited between two layers of charcoal. From August to October 1916, all LBRs were replaced by SBRs.

2.3.3 The French

The French military responded to the tear gases with a pad mask, Tampon P, together with goggles. The first model had one pad impregnated with castor oil and sodium ricinate, and it could protect also against chlorine and bromide. The anticipation of phosgene deployment led to the addition of a second pad impregnated with sodium sulfanilate. This pad was known as Tampon P1. For the protection of the soldiers from HCN that was released by the French against the German army, a third pad impregnated with nickel acetate was added leading to a new mask with the code name Tampon P2. The French army used more than 4.5 million Tampon P masks between August and September 1915. These masks were not efficient for high concentrations or for a long-term usage, since only the part of the pad in front of the mouth was breathable and the chemical were quickly exhausted in this part. The next version of the mask had a cone shaped pad, which was covering both the nose and the mouth. The manufacturing of this Tampon T model allowed almost all the surface of the pad to come in contact with the gases and as a result the time efficiency increased. The first Tampon T masks arrived to the battlefields in the middle of November, 1915. An improved version was produced in January 1916, with a waterproof cover and a redesigned shape for a faster usage. It was referred to as a TN model. By the end of February, around one million of T and 6.8 millions of TN models were produced. On the Tampon masks, goggles were a separate part.

The first attempt from the French to combine the pad inside a one-eyepiece mask that could cover the whole face was the first M2 model. The thicker pad could protect against phosgene up to 6 h, and it was introduced to the battlefields in March 1916. The second M2 model had two eyepieces and three sizes. It was introduced in April 1916, and it was the main face protection medium for the French infantrymen until the middle of 1918. Between March 1916 and November 1918, almost 30 million of all M2 models were manufactured.

Simultaneously with M2 and later with the ARS Gas mask, the French army used also another gas mask, the Tissot Large/Grand model or "APPAREIL T" (Apparatus Tissot). The name originated from the inventor of this breathing respirator apparatus, Dr. Jules Tissot. These masks were used in a mine rescue for a year prior to WWI. The filtration medium was a rectangular metal box that was carried at the back, due to a large size. The box was filled with iron potash and wood chips impregnated with a mixture of sodium bicarbonate and castor oil [25]. The facial part was made from rubber. The inhalation/exhalation system was made of varnished copper tubes. The eyepieces were surrounded by a metal ring and they were glued to the rubber. The most important asset of this mask was a design based on the "Tissot Principle", where the inhaled air flew around the inside part of the lenses prevented water condensation and in this way the problem of fogging was overcame. The defogging of the lenses and the absence of the uncomfortable nose clip and mouthpiece set made the Tissot gas mask the most comfortable and



THE CHRONICLE OF THE EARLY GAS MASKS MODELS

Fig. 2.5 Chronicle of the most important gas masks models and the CWAs' deployment dates until 1917 (Sketches 1–5 and 7–9 by Andrea Silva, sketch 6 by Prof. Andreas D. Jannakoudakis: (Aristotle University of Thessaloniki, Greece))

effective gas mask used during WWI. The delivery of the first 450 masks to the frontlines began in July 1916. In 1916 and 1917 an updated version of the Tissot Large/Grand model appeared [5]. The characteristic fragile "flapper" type outlet valve (Fig. 2.5) was protected with a cylindrical piece, while the rubber material was thicker and was impregnated with boiled linseed oil [25]. Almost one year after the first appearance in the battlefields, the wood chips were replaced with charcoal.

The main drawbacks of the Tissot mask were the size and weight. For these reasons, these masks were assigned to soldiers with critical duties who had fixed positions, like artillery and trench mortar crew, snipers, messengers, medics, combat engineers. In 1917, a new and smaller filtration box was used, and thus, the usage of the mask by infantrymen was possible. This model was known as Tissot Small model or 1917 Tissot. More than 100,000 units of the Large and Small models were manufactured, until the Armistice (November 11, 1918). The Tissot mask is now one of the rarest apparatuses, since almost no units survived, mainly due to the decomposition of the rubber part.

The French army also provided their infantry with a more advanced mask with a changeable filter cartridge in the front of the face mask, similar to the *Lederschutzmaske*. This mask was referred to as ARS Gas mask (Appareil Respiratoire Spécial Modèle 1917) and was first used on the battlefields in November of 1917. A rubber face piece impregnated either with wax or oil had two celluloid eyepieces. Similar to the Tissot mask, the inhaled air flow was directed through the canister to the eyepieces, preventing their fogging. Because of the smaller size than that of SBR, the absence of the uncomfortable noise-clip and mouthpiece, and the anti-fogging property, ARS was established as the most desired gas mask by the soldiers of the Allied forces, and almost 5.3 million of these types of masks were used from November 1917 to November 1918.

2.3.4 The Italians

The Italian army used the French knowledge to manufacture gas masks. The first mask was made of a thick wad of gauze impregnated with hydrosulfate and carbonate soda solution, while the googles were worn separately. It was effective only against chlorine. Many different mask versions were developed later and because of their single purpose use, they were called monovolente. These masks were abandoned after the disaster at Mount San Michele on 29th of June, 1916, where the Austrian army used phosgene. The Italian casualties were more than 2000 soldiers while about 5000 were poisoned [26]. The first multipurpose (polivolente) mask was based on the French TN model. The new mask had the same pad-based setup and separate goggles, but it offered protection against phosgene. The next polivolente model (Z), called a funnel type, was based on the M2 French mask. It was introduced in January 1917 [27], and it covered the entire head with a rubber cloth and later with leather. The inside gauzes presented an improved performance against phosgene, while the goggles were incorporated into the mask. In spite of all alterations, this mask had limited lifetime and inability to protect against newer toxic compounds, such as mustard gas. The polivolente mask models were abandoned and the Italian army started to be equipped with the British SBR British masks during the battle of Caporetto in 1917 (24 October-19 November).

2.3.5 The Russians

The Russian casualties and fatalities from the CWAs were the greatest compared to all other nations. The Russian generals assigned the task of the gas mask development to Nikolay Zelinsky, one of the founder of the theory and application of catalysis [28]. He had reported that ordinary charcoal had a supreme efficiency for the adsorption of organic fumes. Zelinsky, before the war had also studied the production of activate carbons by calcination. Even though Zelinsky had designed the filter system of a mask before the first gas attack by German forces, there were many difficulties in its application as a full face mask. After many trials, the engineer Kummant designed a rubber mask. The first model of the Zelinsky-Kummant mask with the code name "Petersburg", equipped with a round filter hanging from the mask, arrived in battlefields in February 1916, saving the lives of numerous Russian soldiers. The next improved model "Moscow" had a square shaped filtration system. More than 11 million masks were used in the battlefields during WWI. It is worth to mention that most of the modern gas masks use activated carbon as the main desiccant.

2.3.6 The Americans

The United States of America entered WWI after the declaration of the Congress on April 6, 1917. The US army had limited knowledge or experience on toxic gases and gas masks, even though WWI started almost three years before. This was because the updates were coming with a delay from the Western Front. In many cases, the Allied forces intentionally did not reveal the entire picture of the war situation because of fear that it will decrease the willingness of the USA to actively participate in the battles. The first order to produce 25,000 gas masks similar to those of the British Small Box Respirators was placed on May 16, 1917. Twenty thousand copies were ready and shipped to England for inspection in less than a month. Unfortunately, these copies, known as Bureau of Mines Mask, were found as improper for use, since the soda lime granules formed big clusters that were blocking air inlets. Moreover, the rubber face piece was vulnerable to chloropicrin.

In July, the second production resulted in the American Training Gas mask (ATS). This model was almost the same as the first one and never had never been shipped overseas. ATS classified as "experimental model" and was used for training purposes, since the production started before the British army informed the US army that these masks were ineffective. The US army training regulations stated that 9 seconds should be the maximum time to put on/wear the SBRs or ATS masks. The production of this model took less than three months.

The first limited number of soldiers/infantryman (around 14,000), known also as doughboys of WWI, arrived in France on June 1917. Although, the first involvement of the doughboys (First Division) in the battlefields took place on October 21 of that year, owing to time needed for US troops for training. Meanwhile, on July 5,

Table 2.3 The masks and canisters developed during WWI along with the month of their first usage in the battlefields, CWAs targeted, and the chemical composition of the filtration media. (Type of masks: pads with separate goggles (P), Full face mask with pads inside (FP), Full face with drum canister (FC), Full face with the filter separated and connected via tube (FS), and canister only (C). The masks that were never used in battlefields are indicated with asterisk.)

Name		Date introduced	Force	Туре	Designed to protect against	Chemicals
1915	Chlorine attack Apr	il 2015				<u></u>
	German pads	April	Ŧ	(P)	Chlorine	Sodium thiosulfate
	Daily mail pads	May		(P)	Chlorine	Urine or bicarbonate soda
	Black veiling	May	×	(P)	Chlorine, SO ₂ , nitrous fumes	Sodium hyposulfite, glucerine, sodium carbonate, water
	Hypo helmet	June	**	(FP)	Chlorine, SO ₂ , nitrous fumes	Hypo solution (sodium thiosulfate, sodium hyposulfate, glycerin)
	P helmet	July		(FP)	Phosgene, HCN	Hypo solution plus sodium phenate
	Tampon P	Aug		(P)	Chlorine, bromide	One impregnated pad with Castor oil and sodium ricinate
	Tampon P1	Aug		(P)	Phosgene	Tampon P plus a second pad impregnated with sodium sulfanilate for protection against phosgene
	Gummimaske	Sept	Ŧ	(FC)	Chlorine, tear gases	Diatomite and charcoal
	PH helmet	Oct	**	(FP)	Chlorine, tear gases	Hypo solution plus sodium phenate and phenate hexamine
	Tampon P2	Oct		(P)	HCN	As P1 plus a third pad impregnated with nickel acetate
	Tampon T	Nov			tear gases, chlorine	As P2, different mask shape
	Phosgene-Decemb	per 1915				
1916	PHG helmet	Jan	AK	(FP)	Chlorine, tear gases	As PH, plus rubber sponge goggles
	Tampon TN	Jan		(P)	Phosgene, tear gases, chlorine	As T model plus one waterproof cover
	Tampon TN	Jan		(P)	Phosgene, tear gases, chlorine	As T model plus one waterproof cover
	Zelinsk-Kum	Feb		(FC)	Phosgene, tear gases, chlorine	Activated carbon
	Large Box Respirator (LBR)	Feb		(FS)	Phosgene, tear gases, chlorine	Lime-permanganate granules, pumice pieces impregnated with sodium sulpfates and charcoal

(continued)

Table 2.3 (continued)

Name		Date introduced	Force	Туре	Designed to protect against	Chemicals
	M2	Mar		(FP)	Phosgene, tear gases, chlorine	Impregnated pads inside one-eyepiece mask
	11/11	April	H	(C)	Phosgene, tear gases, chlorine	Charcoal granules and Diatomite impregnated with hexamine and potash
	M2 2nd model	April		(FP)	Phosgene, tear gases, chlorine	Two eyepieces instead of one
	Tissot large	July		(FS)	Phosgene, tear gases, chlorine	Iron potash and wood chips impregnated with sodium bicarbonate and castor oil
	Chloropicrin—Aug	ust 1916				
	Small Box Respirator (SBR)	Aug		(FS)	Phosgene, tear gases, chlorine	Charcoal and lime-permanganate granules
1917	Polivolente Z	Jan		(FP)	Phosgene, tear gases, chlorine	Various impregnated pads inside a face piece
	Tissot small	Mar		(FS)	Phosgene, tear gases, chlorine	Iron potash and wood chips impregnated with sodium bicarbonate and castor oil
	11-C-11	June	Ŧ	(C)	Chloropicrin, mustard gas	More charcoal than 11/11
	ATS (Training) *	July		(FS)	Phosgene, tear gases, chlorine	Based on SBR
	Mustard Gas-July	1917				
	Lederschutzmaske	Aug	Ŧ	(FC)	Mustard gas	Waterproof leather embedded in oil instead of rubber
	CE	Oct		(FS)	Phosgene, tear gases, chlorine	Activated charcoal from coconut shells
	ARS	Nov		(FS)	Mustard gas, Phosgene, tear gases, chlorine	Tissot principle, rubber face piece impregnated with oil or wax
1918	RFK	Feb		(FS)	Mustard gas, Phosgene, tear gases, chlorine	Activated charcoal from coconut shells, soda lime granules, and impregnated cotton pads
	AT *	Jun		(FS)	As RFK	Tissot principle
	KT *	Aug		(FS)	As RFK	Tissot principle
	KTM *	Oct		(FS)	As RFK	Tissot principle

1917, the US army established a special expeditionary force for the frontlines in Europe, the American Expeditionary Force (AEF). Large numbers of US troops started to arrive gradually on Europe in 1918. It is worth to mention that the rate of the arrived soldiers per day reached 10,000 by June. AEF experienced the first gas attack close to Pargny (France) on March 16, 1918 [29]. The German army, knowing that the American forces did not have any experience, except an in-door theoretical training consisted of a two hours lecture about the protection against toxic gases and demonstrations of how to use the gas masks, launched various gases. Even though the US infantryman were equipped at the beginning with SBRs, purchased from the British, and with M2 obtained from the French, many soldiers did not manage to put on the masks on time, because they did not realize the presence/deployment of the toxic gases, until it was too late. The soldiers suffered also from the contamination of food.

The updated version of the training mask was the first mask that started in October 2017 to be produced and used in the battlefields by the USA. This Corrected English Model Respirator (CE) had a canvas face piece with two celluloid lenses surrounded by metal rims. The CE masks were more comfortable to wear, since the metal nose clip and the snorkel-like rubber mouthpiece were redesigned. A steel bracket was added in order to protect an ultrasensitive outlet/ exhale valve. The yellow "H" filter canister was also improved, and it was filled predominantly with activated charcoal derived from coconut. An updated version of the CE mask had glass lenses and a more effective protection bracket. Almost two million CE masks were produced and used by AEF until March 1918.

The next version was the gas mask referred to as RFK and named after the designers Richardson, Flory, and Kops. It was the primary WWI gas mask for the troops. It had a wider face piece with a redesigned two-pieces adjustable head strap, and the glass lenses were yellow. The updated green colored "J" canister had a combination of activated coconut-based charcoal with soda lime granules and impregnated cotton pads. It provided less breathing resistance. Over 3 million masks of this version were used from February 1918 until the WWI Armistice. Three more models were developed until the end of the war: Akron Tissot (AT), Kops Tissot (KT), and Kops Tissot Monro (KTM). All of them utilized the advanced Tissot breathing respirator apparatus, eliminating the necessity for the nose clump and mouthpiece. Manufacturing problems limited their production to around 200,000, 335,000, and 2,000 masks of each type, respectively.

The need for a more reliable respirator, which would be based on the adsorption and not on neutralization was clear. Moreover, the increased need for the development of advantageous adsorption materials, that can be applied in various protection media, rose after the deployment of Mustard gas. The ability of this blister agent to penetrate cloths as well as skin, and to exist/last even for weeks in trenches, expanded the necessity of the protection also to uniforms, gloves, and shoes.

A collective chronicle of the most important gas masks models and the CWAs' deployment dates until 1917 is presented in Fig. 2.5. All the masks and canisters

that were developed during WWI along with the month of their first usage in the battlefields, CWAs targeted, and the chemical composition of the filtration media are collected in Table 2.3.

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Chapter 3 Mustard Gas: The King of CWAs

3.1 Mustard Gas

The blistering agent (or vesicant) sulfur mustard (HD), also known as mustard gas or Yperite, can be considered as the king of the battle gases, since it was the most effective and widely used. It caused the largest number of casualties among all CWAs used during WWI. The main component of HD is bis(2-chloroethyl) sulfide (Fig. 3.1). It was synthesized and characterized in 1860 by a British professor, Frederic Guthrie. Although there are prior reports concerning the synthesis of HD as early as 1822, Guthrie was the first one who experienced and mentioned its irritating properties after its contact with his skin. It took 57 years to realize its high toxicity and its potential for a large-scale production. This vesicant has a characteristic rotten odor like mustard plants or garlic, hence the name mustard gas. The initial name, before the attack at Ypres, was lost from the first two letters of the last names of Wilhelm Lommel and Wilhelm Steinkopf, who developed the method for its large-scale production for the German army in 1916. Another crucial reason for the extensive use of HD was its relatively simple synthesis from precursors that were available to the German Empire at the time of WWI.

The name mustard is misleading, since bis(2-chloroethyl) sulfide is a colorless viscous d = 1.2685 g/mL at 25°C), insoluble in water, with a melting point of 14 ° C, and decomposes at 218 °C [1]. Chemically, it is very stable at ambient conditions. Interestingly, German munitions, used in the First and Second World Wars that were dug out at the battlefields some years ago in Belgium, revealed that the agent barely degraded [2]. The reported colored clouds were attributed to the use of impure forms, since in almost all cases HD was utilized as a mixture. The fumes of HD are 5.5 times heavier than air, with a vapor pressure of 0.106 torr at 25 °C.

HD is highly toxic for humans and animals, similar to phosgene and hydrocyanic acid. The most toxic route of exposure is inhalation, but it can also penetrate the skin. HD attacks the respiratory tract, eyes, and skin, acting firstly as irritant and

Fig. 3.1 Bis(2-chloroethyl) sulfide, known as mustard gas (molecular weight 159.07)



afterward as a poison for the body's cells. Its toxicity is associated with the ability to alkylate proteins and rapidly penetrate through a membrane into a living cell, releasing HCl after hydrolysis. The effects of the exposure to HD are revealed gradually. At the first stage, the agent attacks the skin, eyes, and respiratory tract, resulting to blisters. The most common symptoms, which are appearing even hours after the exposure, are the big skin blisters and bloodshot eyes, accompanied by pain. At the second stage, HD attacks the cells of various organs. The victims suffer from coughing up blood, muscle spasms, vomiting, sneezing, necrosis of the blisters' spots, and possible blindness after days. If the victims were exposed to a high amount of HD, the symptoms lead to death within 3 days, caused by heart failure or lung edema. The lethal dose is around 7.5 g of liquid HD for human weight around 160 lbs. The lethality when inhaled in its gaseous form depends on the exposure length and the concentration. On its first use at Ypres, only 5% of the exposed soldiers were finally killed, since the concentration of the mustard gas clouds was low when reached the Allied forces.

Mustard gas became a popular CWA also owing to its ability to contaminate enemy trenches. It remains stable in soil and under average weather conditions. The exposed fields are highly toxic for two to three days, while under very cold conditions mustard gas retains its toxicity even up to months. In many occasions, it can be mixed with nonvolatile solvents in order to extent the contamination of the trenches. Another property of HD is that it can easily penetrate through clothing and thus gas masks do not provide enough protection. The panic, resulting in the breakage of the defense lines, inflicting serious short- and long-term injuries, requirement of a full body protection equipment, and the contamination of the attacked fields for days, established mustard gas as the one of the most used and dangerous CWAs. Another problem associated with its deployment was that the victims exposed to mustard gas could not be moved directly to hospital wards without precautions, since their cloths or even the hair could contaminate the entire ward.

3.2 Mustard Gas Deployment Post the WWI

The deployment of mustard gas was not limited to WWI. Although Italy had signed the Geneva Protocol banning chemical and biological weapons in 1925, the Italian dictator Benito Mussolini ordered in 1935 a bombing against the Emperor Haile Selassie's army with mustard gas. The Italian forces used HD extensively during their colonial campaign in Abyssinia (Ethiopian Empire) from 1935 to 1936. HD was also used during the North Yemen Civil War (1962–1970) by Egyptian forces
against the Yemeni monarch, in order to support a coup. An Iraqi Army, under the orders of Saddam Hussein, also used mustard gas bombs against the Kurdish people, in March 1988. Mustard gas remains a standing threat, since it can be easily produced by terrorists. Even after more than 150 years of its discovery and almost 100 years after its first usage, no antidote has been discovered, since the first step of its activity, alkylation, takes place extremely rapidly [3]. Some internal injuries can be controlled by medicines. For example, the lung injuries can be treated with bronchodilatory treatment, while the eye injuries can be controlled with antibiotics. Skin injuries, that can be second- and third-degree chemical burns, can be controlled with soapy water and small amount of bleach (saline solution). A plastic surgery may be necessary after the skin injuries are healed.

3.3 Proposed Decomposition Pathways of HD

The most common pathways of the HD decomposition are collected in Fig. 3.2. Hydrolysis and dehydrohalogenation are the foremost desired reaction paths reported for various neutralizing agents and adsorbents; however, both result in the



Fig. 3.2 Detoxification pathways of HD (asterisks mark toxic compounds)

formation of toxic products. While hydrochloric acid forms in both pathways, hydrolysis forms also thiodiglycol (TG). The formed chloride anion during the reactive adsorption can poison the active centers of the absorbents. The usage of a photoreactive catalyst leads to the formation of molecules with an increased molecular weight, as a result of the recombination of the formed radicals. These compounds are not desirable even if they are significantly less toxic. Selective partial oxidation leads to the sulfoxide derivatives that are considered as nontoxic, while the sulfone derivatives from the full oxidation have vesicant properties. For that reason, the retention of the toxic products (HCl and TG) and a selective partial oxidation was, is, and will be an ultimate target for the developing of advance materials for the efficient mustard gas detoxification.

3.4 The Surrogate of Mustard Gas

Because of the extremely high toxicity of CWAs, several surrogate-analogs and derivatives have been used for research studies focused on the development of decontamination technologies. The most commonly used surrogate for HD is the half mustard gas, 2-chloroethyl ethyl sulfide (CEES, Fig. 3.3), which is less toxic than HD. CEES contains the same ClCH₂CH₂S-group as mustard gas does. This moiety is responsible for its toxicity. It has a boiling point of 156 °C, and its density is 1.07 g/mL at 25 °C.

3.4.1 Detoxification Pathways of the Mustard Gas Surrogate, CEES

The most common reported pathways of CEES detoxification are collected in Fig. 3.4 Hydrolysis leads to hydroxylated sulfide (hydroxyethyl ethyl sulfide, HEES), while dehydrohalogenation leads to vinyl sulfide (ethyl vinyl sulfide, EVS). These two pathways are the foremost reported in the literature for the interactions of metal oxides with CEES in a solution. In both cases, HCl is simultaneously formed. The latter has almost equal toxicity to that of CEES. The formed chloride anion during the reactive adsorption can poison the active centers of the absorbents, leading to a decrease in the performance. The oxidation of CEES can lead to the formation of sulfoxides and sulfones. The latter are highly toxic, and for that reason only selective oxidation is desirable. Many photoreactive catalysts lead to di- or poly-sulfides with increased molecular weight compared to CEES, as a result of the

Fig. 3.3 2-chloroethyl ethyl sulfide (CEES), known as half mustard gas (Mw: 124.63)

∠S∖ CI~~



Fig. 3.4 Detoxification pathways of CEES reported in the literature (asterisks indicate toxic compounds)

cleavage of the S–C bond by the involvement of radicals and their further recombination to various products/combinations. Moreover, cleavage of the S–C bond of CEES followed by hydrolysis or oxidation can lead to small fragments, such as ethanol, acetaldehyde, chloro-acetaldehyde, ethyl sulfide. These compounds are nontoxic and volatile, and due to their small sizes, they can retain inside the pore system of the filtration materials.

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Chapter 4 Current Protection Against CWAs

4.1 Whetlerites: The Improved Military Activated Carbon

Immediately after the first vast scale deployment of CWAs in battlefields, the development of protection medias for the soldiers, and predominantly gas mask, became an important research target. The first trials were based on filtration means covering the mouth and nose, impregnated with various solutions that chemically neutralized the toxic compounds. The versatility in CWAs and the fear of a possible deployment of new CWAs led quickly to the development of the "ideal" respiratory system: a full face mask with a canister for the inhalation, which protects simultaneous the respiratory tracks and the eyes. The unique property of the activated carbons to physically adsorb various organic compounds led gradually to its establishment as the main filler of the canister use by the Allied forces. Nevertheless, that development took almost a year after the first chloride attack by the German army. The latter adopted this system for the protection of all soldiers four months after the first vast scaled attack with chlorine in April 1915. Interestingly, a similar gas mask system was designed in 1850 by John Stenhouse at Glasgow [1], and took long time for its application in battlefields.

At the beginning, the adsorption of the toxic gases was based on physisorption by Van der Waals forces in the highly porous system of the wood-based charcoal. These carbons have mainly micropores with limited number of weakly reactive centers, and as a result, they did not show so high adsorption capacities for larger toxic molecules. The importance of increasing the adsorption ability of the activated carbons led to the application of impregnated carbons with active substances. In this way, these active impregnates can strongly retain toxic molecules via chemical bonds, or catalytically decompose them to smaller molecules, which can further get physically adsorbed by the carbon phase. The main drawback is that the adsorption ability of the carbon canisters is directly proportional to the amount of carbon and its impregnation extent. The first impregnated carbon for military use was developed by J.C. Whetzel and E.W. Fuller, and based on their names, it was called Whetlerite [2]. There are

numerous impregnation versions, but nowadays Whetlerites commonly represent an entire family of impregnated carbons for military use. Impregnated with cooper Whetlerite A was a very first type of those materials used during WWI was. The most popular type was the ASC whetlerite carbon, which contains Cu, Cr and Ag. Various other non-toxic, non-carcinogenic metals were tried, mainly to replace the chromium. The ASZMT type, which contains Cu, Ag, Zn, and Mo, showed the best performance with an additional impregnation with triethylene diamine [3]. The combination of metals provides the ability to Whetlerites to act as catalysts and detoxify a wide range of CWAs. Whetlerites are used today as fillers in the military mask canisters.

4.2 Research on New Adsorption/Detoxification Materials

The challenge in the material science is to develop a new generation of materials, which will have an improved detoxification performance per volume compared to the existing carbon-based filters, in order to be applied to smaller and lighter products. Such materials could be used not only in the gas mask, but also in the uniforms and in industrial, medical and military applications. In the last decades, many materials have been studied for the CWAs decontamination, and especially against Mustard gas or its surrogate, CEES. The primary target is to strongly retain toxic molecules on the surface and to rapidly, selectively, and catalytically decompose them to smaller and/or non-toxic compounds.

A direct comparison of the addressed in the literature materials' performance as CEES reactive adsorbents is difficult, due to the differences in experimental setups. Most of the studies focused on the adsorption performance, detoxification kinetics, and decomposition pathways in solutions, using various solvents such as carbon tetrachloride, heptane, methanol, pentane, tetrahydrofuran, chloroform, and dichloromethane [4–13]. The materials that attracted mostly the interest of the researches are predominantly metal-based materials, such as single or mixed oxides/hydroxides, metal organic frameworks (MOFs), and zeolites. A summary of the performance of various tested materials, the conditions of the adsorption tests, the main findings, and the detected reaction products are collected in Table 4.1.

In this book, we have collected the most recent research results on the interactions of the vapors of the surrogate of mustard gas, CEES, with various bulk metal oxides/hydroxides, their composites with graphite oxide GO and/or nanoparticles (Au or Ag), on nanopowders, mixed (hydr)oxides, composites of metal organic frameworks and oxidized graphitic carbon nitride nanospheres, as well as carbon cloths. Modification of textiles (cotton or carbon based) is also mentioned. Finally, "smart" textiles that can simultaneously adsorb, degrade, and sense are introduced.

Material	Conditions	Observations	Reaction products	Ref
Cu-BTC MOF	Solution of HD and CEES in carbon tetrachloride.	Porous structure plays a crucial role. The removal kinetics follows the first order reaction	TG, HEES	[4]
CaO nanosize	Direct interactions of a powder with liquid HD	Interactions resulted in 80% elimination and 20% hydrolysis.	TG, DVS, CEVS	[5]
CuO nanoparticles calcined	Direct interactions of a powder with liquid HD	Calcination temperature alters an adsorption capacity and the nature of degradation products.	TG, DVS, HEVS, CEVS	[6]
MgO nanoparticles	Solution of CEES in heptane, methanol pentane, and tetrahydrofuran	Crystal shape and surface area affect a decontamination performance. The highest reaction rates obtained in pentane.	EVS, HEES	[7, 8]
VO ₂ Porous nanotubes	Direct interactions of a powder with liquid CEES and with its solution in pentane.	Degradation is faster in solution than when in a direct contact with droplets.	HEES, sulfoxide, EVS	[9]
Zr(OH) ₄	Direct interactions of a powder with HD	Water-insoluble HD undergoes slow hydrolysis on hydrophilic zirconium hydroxide	TG and vinylic products	[10]
ZnO nanorods and commercial ZnO	Solution of HD in chloroform	Even with almost equal surface areas, ZnO nanorods were more efficient in decomposition than was commercial bulk ZnO.	TG, DVS	[11]
MnO ₂ nanobelts	Solution of HD and CEES in dichloromethane	Only hydrolysis took place.	DG, HEES	[12]
TiO ₂	Vapors CEES	26 compounds extracted from the surface after the adsorption in UV, while only seven detected in dark.	26 compounds	[14]
UiO-66/ UiO-67	Unbuffered aqueous solutions of CEES	Hydrolysis was a predominant detoxification pathway	HEES	[15]
NU-1000	UV LED used for the formation of ${}^{1}O_{2}$	Reusability of MOF led to increased detoxification rates	CEESO	[16]

Table 4.1 Highlighted studies on the HD and/or CEES removal on various materials

^aAbbreviations: thiodiglycol (TG), hydroxyethyl ethyl sulfide (HEES), divinyl sulfide (DVS), hydroxyethyl vinyl sulfide (HEVS), ethyl vinyl sulfide (EVS), chloro-ethyl vinyl sulfide (CEVS), divinyl sulfide (DVS), and 2-chloro-ethyl ethyl sulfoxide (CEESO)

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Chapter 5 New Approaches in the Detoxification of CWAs

5.1 Zinc (Hydr)Oxide-Based Multifunctional Nanocomposites



In this subsection, the results reported in Refs [1] and [2] are included, with permission from Elsevier.

5.1.1 One-Pot Wet Precipitation of Zinc (Hydr)Oxide

5.1.1.1 The Role of the Base Addition Rate

An important task of our research was to determine the synthesis conditions leading to the formation of pure zinc hydroxide of high porosity. For this, a one-pot precipitation method was used with water as a solvent, sodium hydroxide as base (in a molar ratio 1:2 ZnCl₂ to NaOH), and zinc chloride as a source of the metal. It was previously reported that alteration of the solution pH, temperature, and the base

© Springer International Publishing AG 2018 D. A. Giannakoudakis and T. J. Bandosz, *Detoxification of Chemical Warfare Agents*, https://doi.org/10.1007/978-3-319-70760-0_5 addition rate to the metal salt solution can result in different features of metal (hydr) oxides. Thus, in this way, the structural and morphological properties such as the porosity and particle size can be significantly adjusted.

The addition of the base to the zinc chloride solution was occurred following two ways. In the first approach, the base was added dropwise with a controlled rate. Even though a wide range of different addition rates were tried, the precipitations received with rates 1, 2, 10, and 20 mL/min were analyzed. After the complete addition of the base, subsample of the precipitation was thermally treated at 95 ± 5 °C for 1 h. In the second approach, the base was added rapidly in addition to the salt solution. The received precipitation was afterward aged under stirring in room temperature for 10 and 30 min, 2, 12, 24, and 48 h.

5.1.1.2 Structural and Morphological Characterization

The crystallinity and purity of the synthesized samples were analyzed using the powder X-ray diffractions. The characteristic diffraction peaks of hexagonal ZnO (würtzite), orthorhombic ε -Zn(OH)₂ (wülfingite), and orthorhombic γ -Zn(OH)₂, from the standard cards JCPDS 36-1451 [3, 4], JCPDS 38-0385 [5], and PDF 00-020-1437 [6], respectively, are collected in Fig. 5.1.

The XRD patterns of the samples prepared by dropwise addition of the base are collected in Fig. 5.2. In the sample synthesized at a rate of 2 mL/min, orthorhombic ϵ -Zn(OH)₂ is the main crystallographic phase, since the diffraction peaks at 20.2, 20.9, 27.2, 27.7, 32.8, 39.5, 40.8, 42.1, 52.4, 57.8, 59.5, and 60.4 20 are matching perfectly with the JCPDS Card no. 38-0385. However, the minor reflections, located at 31.7, 34.4, 36.2, and 47.6 20, correspond to traces of würtzite structure of zinc oxide, while diffractions linked to γ -Zn(OH)₂ are not detected only in this sample. The rest of the samples prepared with rates 1, 10, and 20 mL/min showed, except the diffraction peaks of the ε -Zn(OH)₂, the peaks at 11.5, 28.5, 30.7, and 34.8 2 θ , which are related to the γ -Zn(OH)₂ structure. Their intensities were different. The result of the thermal treatment of the precipitation after the complete addition of the base for 1 h at 95 °C revealed that the crystal structure change upon heating to well-crystallized ZnO, as can be seen for the pattern of the sample prepared with rate of 2 mL/min and further thermal treatment at 95 \pm 5 °C for 1 h. The same pattern was found for the rest of the trials and even for lower temperatures (60 \pm 5 °C). Based on these findings, it can be concluded that the one-pot







Fig. 5.2 X-ray diffractograms of the sample obtained with a controlled addition of the base and the one prepared with a rate of 2 mL/min and further thermally treated at 95 ± 5 °C for 1 h

in situ wet synthesis method is very sensitive and the base addition rate plays a crucial role for the development of the final crystal structure.

The differences in the morphology and shape of crystal structures as a result of a different addition rate are seen in SEM images collected in Fig. 5.3. In the SEM image of the sample prepared with a rate of 1 mL/min (Fig. 5.3a), two different crystallographic phases are detected. The one with plate-like shape is linked to the gamma phase of zinc hydroxide, while the octahedral-shaped particles correspond to the ϵ -Zn(OH)₂. As revealed from the XRD pattern, the sample prepared with a rate of 2 mL/min showed mainly the existence of the octahedral-shaped ϵ -Zn(OH)₂ particles (Fig. 5.3b). Further increment of the addition rate led to the conversion of the latter particles, to the γ -Zn(OH)₂ phase (Fig. 5.3c, d).

The X-ray diffractograms of the sample obtained with the rapid addition of the base, followed by various aging periods, are collected in Fig. 5.4. The powder X-ray diffractograms for the entire series of these samples indicate that the crystallographic phase is that of hexagonal zinc oxide, since the three most intense peaks at 31.7, 34.4, 36.2, and 47.6 2θ match perfectly with the JCPDS Card no. 36-1451. With the aging periods over 2 h, traces of willingite were found. They entirely disappeared for the precipitate aged for more than 48 h. Interestingly, the diffractograms of the samples aged for more than 24 h showed decreased intensities of the characteristic peaks of the ZnO phase. Since the peak at 34.4 2θ decreased most in its intensity, this can be linked to the partial destruction of the well-defined hexagonal structure. The broadening of the peaks is due to the decrease in the particles' size.



Fig. 5.3 SEM images of the sample obtained with a controlled addition of the base



Fig. 5.4 X-ray diffractograms of the sample obtained with a rapid addition of the base and aged for various periods

The SEM image of sample aged for 2 h (Fig. 5.5a) shows mainly flower-like nanoscaled particles linked to the ZnO phase. Defected octahedral particles of ε -Zn (OH)₂ are also visible. This finding agrees with the results of the X-ray diffractogram, where two distinguished crystals phases are detected. In the samples aged for 12 h, the size of the both above-mentioned phases decreases (Fig. 5.5b). 24 h resulted in the conversion of the flower-like particles to rice-like particles (Fig. 5.5c). Further aging leads to the formation of spherical nanoparticles with significantly smaller size (Fig. 5.5d).

5.1.1.3 The Influence of the PH

Since the main target was to obtain zinc hydroxide, for all samples the NaOH/ZnCl₂ molar ratio was 2:1, based on the targeted reaction: $ZnCl_2 + 2$ NaOH \rightarrow Zn $(OH)_2 + 2$ NaCl. The precursor solution had an initial pH equal to 5.9 ± 0.2 . In the case of the dropwise addition of the base, the pH of the solution never went beyond 9.8. On the other hand, the pH reached 11.4 ± 0.2 , when the base was added rapidly. The addition of the base to the zinc precursor solution resulted in the



Fig. 5.5 SEM images of the sample obtained with a rapid addition of the base and aged for various periods of time



Fig. 5.6 Schematic representation of the possible reaction pathways for the formation of $Zn(OH)_2$ and ZnO. (Reprinted from Ref. [1], Copyright 2017, with permission from Elsevier)

formation of various intermediate aquocomplexes, such as $[Zn(OH)_4]^{2-}$, [Zn $(OH)_3$ ⁻¹, and $[Zn(OH)_x(H_2O)_y]^{2-x}$ [7, 8]. The precipitation of stable $Zn(OH)_2$ is favorable over that of ZnO, if the pH is maintained between 6.5 and 10 at room temperature during the whole synthesis. At these conditions, the intermediate aquocomplexes condensed, forming zinc hydroxide. On the contrary, the increase of the pH to more than 10.8, as in the case of the rapid addition, results initially in the simultaneous formation of ZnO and Zn(OH)₂. The latter phase is unstable and can get converted to ZnO via two possible pathways [7]. The first involves dissolution of the zinc aquocomplexes, which then reprecipitate as the less soluble and more stable ZnO in the whole pH range [8]. The second pathway involves a solid-state transformation caused by dehydration. It can be concluded that the formation of ZnO or Zn(OH)₂ depends on the kinetics of the precipitation and can be controlled by adjusting the pH value. The proposed mechanism (Fig. 5.6) is in agreement with studies addressing the formation of ZnO by decomposition of Zn $(OH)_2$ [5, 7, 9, 10]. It also further supports previous findings on the formation of different precipitates by changing the mixing time and thus the pH gradient [8, 9].

5.1.1.4 Conclusion

The results presented in this chapter show that by controlling the addition rate of the precipitation agent (NaOH) to a zinc chloride solution, either zinc hydroxide or zinc oxide can be obtained. Slow rates result in the formation of orthorhombic particles of $Zn(OH)_2$, while rapid addition leads to the formation of ZnO. The main factor, which regulates the final structural form, is the pH. In the case of the rapid addition, the pH rises above 10.8 after the addition of the base, while the pH during the dropwise addition of the base remained lower than 9.8. The XRD and SEM analyses show the clear structural differences between samples.

5.1.2 Zn(OH)₂ Versus ZnO: The Key Role of the Hydroxyl Groups

5.1.2.1 Introduction and Materials

In order to compare the adsorption and photocatalytic performance, as well as to determine which factors play the most crucial role, two samples were chosen. The first one was the one prepared with a dropwise addition rate of 2 mL/min. It was chosen because it consists of zinc hydroxide phase. This sample is referred to as ZnSA. The second selected material was obtained with the rapid addition and with 2-h aging. It predominantly consists of the zinc oxide nanoflower-like particles. This sample is referred as ZnRA. For the sake of comparison, commercial ZnO nanoparticles were used as a reference material, and it is referred to as ZnO–C.

5.1.2.2 Structural, Chemical, and Optical Characterizations

The diffractograms of three chosen samples are collected in Fig. 5.7. The XRD patterns of the sample synthesized at the slow base addition rate (ZnSA) indicates zinc hydroxide as the main crystallographic phase, while the minor diffraction peaks, located at 31.7, 34.4, 36.2, and 47.6, correspond to traces of würtzite structure of zinc oxide. The diffraction peaks of the sample prepared with a rapid addition of the base correspond to würtzite. The presence of ε -Zn(OH)₂ crystals is also noticed, but in a limited quantity. The pattern of the ZnO–C matches perfectly with the one of würtzite.



Fig. 5.7 X-ray diffraction patterns for the initial samples. (Reprinted from Ref. [1], Copyright 2017, with permission from Elsevier)

The calculated crystallite sizes, using the Scherrer equations [11], found 48.6, 11.8, and 15.1 nm for ZnSA, ZnRA, and ZnO–C, respectively.

ZnSA and ZnRA differ markedly in their pore structure. The total pore volumes and surface areas are summarized in Fig. 5.8. ZnSA has almost ten times higher total pore volume than that of ZnRA. The surface area of the former sample is also 350% higher than that of ZnRA. ZnO–C has a mesoporous structure. The total pore volume is 20% lower than that of ZnSA, but more than six times higher than that of ZnRA.

The nitrogen adsorption isotherms are of Type II and clearly indicate the mesoporous nature of our materials (Fig. 5.9) [12]. This is an important feature and might play a crucial role in the CEES reactive adsorption process [13, 14]. The observed limited H3-type hysteresis reveals the existence of not-complex-shaped



Fig. 5.8 Comparison of the porous structure parameters calculated from the nitrogen adsorption isotherms. (Reprinted from Ref. [1], Copyright 2017, with permission from Elsevier)



Fig. 5.9 Nitrogen adsorption isotherms

pores [12]. The simple shape and large size of the pores is expected to allow the penetration of the CEES molecules to the reactive sites.

The well-crystallized micrometric size particles of ε -Zn(OH)₂ with a rhombic octahedral shape can be seen at the SEM images of ZnSA (Fig. 5.10a) [8, 9, 15]. Moreover, the limited quantity of the ZnO phase is also revealed, with platelets-like particles of similar sizes (Fig. 5.10a). In the case of ZnRA, flower-like zinc oxide particles are the predominant crystallographic phase, with a size of about 0.5–1.2 µm (Fig. 5.10c). This is in agreement with the XRD results. Besides the oxide phase, the rhombic octahedral shape particles of ε -Zn(OH)₂ were also detected as a minor phase (Fig. 5.10d). The commercial zinc oxide consists of the aggregations of spherical nanoparticles with sizes in the range from 40 to 180 nm (Fig. 5.10e, f).



Fig. 5.10 SEM images of ZnSA (**a**, **b**), ZnRA (**c**, **d**), and ZnO-C (**e**, **f**). Red (false) color—the ε -Zn(OH)₂ particles, and blue (false) color—the ZnO nanoflower-like particles. (**a**, **b**, **c**, and **d** images are reprinted from Ref. [1], Copyright 2017, with permission from Elsevier)

The FTIR spectra of the samples studied are collected in Fig. 5.11. The intense and sharp bands at 715 and 900 cm⁻¹ in the spectrum of ZnSA are assigned to the out-of-plane bending and vibration modes of the OH groups, while the one at 830 cm⁻¹ is assigned to the –OH deformation [16]. The Zn–OH bending and twisting vibrations are seen as the bands at 1040 and 1090 cm⁻¹, respectively [7, 17]. The band at 1390 cm⁻¹, with a small shoulder at 1360 cm⁻¹, and the band at 1500 cm⁻¹ are linked to the vibrations of hydroxyl groups from the zinc hydroxide and water. The broad band between 2950 and 3350 cm⁻¹ with a maximum at 3240 cm⁻¹ is assigned to the OH groups of the inorganic phase, while the band at 3450 cm⁻¹ is assigned to the OH groups of water molecules [7].

A different pattern of the FTIR spectrum was received for ZnRA. The twisting and bending vibrations of $Zn(OH)_2$ are totally absent, while the bands related to the out-of-plane bending and vibration modes of the OH groups at 715 and 900 cm⁻¹ have rather small intensities. The broad band between 2950 and 3350 cm⁻¹ and the band representing water at 3450 cm⁻¹ are also of a small intensity. The existence of



Fig. 5.11 FTIR spectra for the ZnSA, ZnRA, and ZnO-C samples. (Reprinted from Ref. [1], Copyright 2017, with permission from Elsevier)

the bands related to hydroxyl groups can be linked to the limited impurities of the zinc hydroxide phase, as detected by X-ray diffraction. This is in a perfect agreement with the reported FTIR spectra of zinc oxide synthesized by the thermal decomposition of zinc hydroxide, where the final pH of the precipitation was near to 11 [7]. In the case of ZnO–C, the nonexistence of the bands associated with the OH groups confirms it highly purity.

Potentiometric titration method was used to determine the quantity and quality of surface functional groups [18, 19]. The pK_a distributions for our samples are collected in Fig. 5.12. Two types of groups are identified: those with pK_a from 7 to 8 and those with pK_a above 10. The first ones are associated with bridging oxygen groups, and the second ones, with terminal hydroxyl groups [20]. The presence of the terminal hydroxyl groups of ZnSA at higher pK_a than those of the other two samples indicates a stronger basic character of this sample, which is probably caused by their different chemical environment. It can be clearly seen that the amount of both types of groups is higher on the surface of ZnSA than on that of ZnRA. The terminal OH groups on ZnSA, while the later sample has 27% more bridging groups than ZnRA. The numbers of the terminal and bridging groups of the commercial zinc oxide are 62 and 84% smaller, respectively, in comparison with ZnSA. The higher amount of the bridging groups in the case of ZnRA compared to those on ZnO–C can be linked to the zinc hydroxide impurities.

The optical properties were evaluated using UV–Vis–NIR diffuse reflectance spectroscopy. The received spectra are collected in Fig. 5.13a. The highest photon absorption in the whole electromagnetic spectrum was obtained for ZnRA. It dramatically increases as the wavelength approaches the UV range. The absorption



Fig. 5.12 pK_a distributions for the samples studied. (Reprinted from Ref. [1], Copyright 2017, with permission from Elsevier)



Fig. 5.13 a UV–Vis–NIR spectra of the samples, **b** $[F(R_{\infty})hv]^2$ versus photon energy. The lines show the cutoff used to calculate the band gap energy. (Reprinted from Ref. [1], Copyright 2017, with permission from Elsevier)

spectra of the ZnSA and ZnO–C follow the same pattern, while the absorption of ZnSA is intensely lower in the UV range. The band gaps (E_g) were calculated from the UV–Vis–NIR spectra [13]. The extrapolation of the linear fit of the plot of [$F(R\infty)hv$]² versus the photon energy (hv) is provided in Fig. 5.13b. The estimated band gaps are 3.22, 3.05, and 2.98 eV for ZnSA, ZnRA, and ZnO–C, respectively. The values of ZnO–C and ZnRA are in the range of other values reported for zinc oxide in the literature [21], while E_g of ZnSA represents a typical value found for zinc (hydr)oxides [22, 23]. The wide band gap in the visible range is an advantage of our materials, since this characteristic is beneficial for application as photocatalyst and optical devices [24].

5.1.2.3 Adsorption Performance: The Role of the Visible Light Irradiation

The materials were evaluated as CEES reactive adsorbents. The weight increase after 24-h exposure to CEES vapors was recorded. The weight increases represent the capacity (Q_{ads}) of the samples to retain CEES and/or its surface reaction products. The values are reported as mg of weight increase per gram of material. The results obtained with irradiation from the solar simulator and in the dark (D) are shown in Fig. 5.14.

The highest adsorption capacities were recorded for ZnSA, which are 263 and 120% higher compared to ZnSA under light and in dark, respectively. Only the former sample showed higher weight uptake of about a factor of two under light than that in dark. This is an evidence of this sample photoactivity. Both ZnO–C and ZnRA showed the same weight uptake at light exposure and in dark. The measured



Fig. 5.14 Adsorption capacities measured under the light exposure from a solar simulator and in dark

capacity at light of the commercial sample is only the half than that of ZnSA, but almost double of the capacity measured on ZnRA. It is worth to mention at this point that even though the density of the light beam not measured, tests at different distances between the solar simulator and the closed adsorption system were attempted, as well as tests under ambient light. In all cases, the capacities showed equivalent values with those reported in Fig. 5.14. This indicates that ZnSA, even at low light exposure, is photoactive.

5.1.2.4 Role of the Textural Parameters

The correlation of the capacity on the structural features (surface area and total pore volume) under light irradiation and in dark is shown in Fig. 5.15. The dependence of the capacity on the structural features shows a linear trend for the experiments held in dark. On the contrary, the correlations are weaker for the capacities measured under light exposure. The total pore volume plays the most crucial in the extent of the adsorption in dark conditions, since the correlation coefficient is 0.99. This can be linked to the penetration of CEES molecules into the porous structure and its further retention by weakly forces. It is possible that the formed surface reaction products are to be retained on the surface with chemical bonds, besides the weakly physical forces.



Fig. 5.15 Dependence of the amount adsorbed on the surface area (left) and the total pore volume (right) under the light exposure and in dark

5.1.2.5 Role of the Surface Chemistry

The dependences of the weight uptake on the number of the terminal and bridging groups are collected in Fig. 5.16. A linear trend with $R^2 = 0.97$ is revealed only in the case of the terminal hydroxyl groups under light irradiation. This trend is stronger compared to the correlation between the weight uptake and the porosity in the case of the experiments held under light. It is important to point out that no linear trend between the weight uptake and the number of bridging groups was



Fig. 5.16 Dependence of the amount adsorbed on the terminal groups (left) and the bridging groups (right) under light exposure and in dark

found. These results suggest a key role of the hydroxyl groups, especially for the extent of photoactivity. They also seem to be important for the retention of CEES molecules on the surface. ZnSA has the highest surface area and number of terminal hydroxyl groups, and for that reason, it revealed the highest adsorption performance even in dark. The positive role of terminal OH groups during the reactive adsorption of actual vapors of CWAs on zirconium hydroxide was previously reported [25]. Calcination of $Zr(OH)_4$ led to a decreased reactivity, due to the transformation to ZrO_2 .

5.1.2.6 Characterization of the Exhausted Samples

In order to evaluate the adsorption mechanism, thermal analysis was performed on the exhausted samples, with simultaneous GC analysis of outgases. The differential thermal gravimetric (DTG) curves of the initial and exhausted samples, under light for 24 h, are collected in Fig. 5.17. Three peaks are revealed at the DTG curve of the initial ZnSA. The first one at 140 °C is linked to the removal of the physically adsorbed water (weight loss 7.9%), and the second one at 225 °C is attributed to the removal of the structural water molecules (weight loss 8.9%) [15]. The broad and low intensity peak with a maximum at 450 °C can be assigned to the total dehydroxylation of Zn(OH)₂ to ZnO (weight loss 6.1%) [26]. Combination of the last two weight losses leads to 15%, which is in good agreement with the theoretical weight loss for the transformation of hydroxide to the oxide zinc phase (18%). The small difference can be linked to the small content of zinc oxide, as revealed from the XRD analysis. The DTG curve of ZnRA showed similar pattern, but with considerably lower intensities of all peaks and a total weight loss only 3.9%. Since ZnO is thermally stable up to 1000 °C, the peaks at 225 and 450 are assigned to the limited amount of the zinc hydroxide in this sample. This is in good agreement with the XRD results. Moreover, the lower intensity of the peak linked to the removal of the weakly adsorbed water molecules suggests a marked hydrophobicity. The DTG curve of ZnO-C clearly indicates the high purity of the oxide phase, since no peaks related to dehydration or dehydroxylation were observed. The total weight loss for this sample was 2.9%.

Three new peaks are revealed on the DTG curves of the samples exposed to CEES under light irradiation, at 160, 300 °C, and at the temperature higher than 760 °C. The m/z thermal profiles of the exhaust gases during the thermal analysis are collected in Fig. 5.18. Table 5.1 collects the names, chemical formulas, abbreviations, and the characteristic mass-to-charge ratios based on which the identifications of the surface reaction products were carried out. The MS thermal profiles of the saturated organic compounds, such as CEES, HEES, or EES (m/z: 75, 63, 61, 47, 29) [27], and the unsaturated product, such as EVS (m/z: 88, 73, 60, 59, 27), showed two peaks with a maximum at 160 and 300 °C [28, 29]. The decomposition of the adsorbed molecules at two different temperatures suggests two energetically diverse adsorption sites. The decomposition of the weakly adsorbed molecules takes place at lower temperature (160 °C), while the



Fig. 5.17 DTG curves in helium for initial and exhausted under light irradiation ZnSA, ZnRA, and ZnO-C. (Reprinted from Ref. [1], Copyright 2017, with permission from Elsevier)

decomposition of the strongly adsorbed molecules—at 300 °C. The comparison of the intensities suggests that in the case of ZnSA, both adsorption sites are favorable. The weight loss which occurred above 750 °C can be linked to the decomposition of the formed ZnCl₂ species during the reactive adsorption [30] and/or to the reduction of zinc oxide to Zn⁰ (boiling point 907 °C) by the carbonaceous phase [31]. The traces of the latter phase might be formed during the thermal analysis (charring of organic compounds). The total weight loss in the case of ZnSA was 28.3%, and it is 5.1% higher than the total weight loss recorded for the initial



Fig. 5.18 m/z thermal profiles (in helium) for the fragments related to CEES, EES, and/or HEES (a) and EVS (b) for the exhausted ZnSA under light (L) and in dark (D) and for the ZnO-C under light (L). (Reprinted from Ref. [1], Copyright 2017, with permission from Elsevier)

Name	Linear formula	Abbreviation	Characteristic
			mass-to-charge
			ratio (m/z)
2-chloroethyl ethyl sulfide	CH ₃ CH ₂ SCH ₂ CH ₂ Cl	CEES	75, 63, 61, 47, 29
2-hydroxyethyl ethyl sulfide	CH ₃ CH ₂ SCH ₂ CH ₂ OH	HEES	75, 63, 61, 47, 29
Ethyl vinyl sulfide	CH ₃ CH ₂ SCH=CH ₂	EVS	88, 73, 60, 59, 45, 27
Ethyl sulfide	CH ₃ CH ₂ SCH ₂ CH ₃	EES	75, 63, 61, 47, 29

Table 5.1 Details on the detected compounds on the surface

sample. This difference is in a good agreement with the amount adsorbed (Fig. 5.14).

Less pronounced differences exist between the DTG curves of the initial and exhausted ZnRA. The three new peaks are at the same positions as those discussed above for ZnSA. The weight loss of the exhausted sample was only 1.4% higher compared to the weight loss of the initial sample. The small weight uptake of ZnRA

limits the detections of m/z in the exhaust gases. The m/z thermal profiles of exhausted ZnO–C were recorded, and the new peaks on the DTG curve match those of ZnSA. The only noticeable difference is that the saturated products are adsorbed on the surface preferably by weak forces, since the intensity of the peaks at the m/z thermal profile is greater at low temperatures. The total weight loss on ZnO–C exposed to CEES is 2.5% larger than that of the initial sample.

The m/z thermal profiles of the ZnSA sample exhausted in **dark** revealed only the decomposition of CEES molecules that were strongly adsorbed on the surface. The m/z thermal profiles of EVS did not show any peak. This suggests that the light irradiation promotes the dehydrohalogenation of CEES to EVS, due to the photoreactivity of ZnSA. The m/z thermal profiles of the exhausted in dark ZnO–C showed limited intensity of the peaks related to EVS.

5.1.2.7 Analysis of the Extracts

The extraction of the species adsorbed on the surface of the exhausted samples was done with acetonitrile as a solvent. The extracts were analyzed by GC-MS and MS-MS. For all samples exposed to light, the main compound detected at the extracts was EVS. Only in the case of ZnSA, the hydrolysis product 2-hydroxyethyl ethyl sulfide (HEES) was also detected. This is strong evidence that the hydroxyl groups play a key role in the reactive adsorption of CEES. It is important to mention that no oxidation products, such as sulfoxide or sulfone, were detected in the extracts, for all the tested materials. In the literature, the degradation products that resulted from the oxidative ability of various metal oxides have been reported [32–34]. In our case, EVS detection was limited in the extracts obtained from the sample exposed to CEES in dark. This supports the results of the TA-MS analysis on the photocatalytic reactions involved during the reactive adsorption and/or on the enhanced reactivity due to an exposure to light. The lack of detection of other products demonstrates the favorable production of EVS, especially upon light irradiation.

Limited trace of CEES was found in all exhausted samples. Since the CEES presence was supported by the TA-MS analyses, its absence during the analysis of the extracts indicates even the inability of the acetonitrile to efficiently extract the CEES from the materials, due to the strong adsorption on the surface.

5.1.2.8 Adsorption Mechanism

The calculated band gaps support the hypothesis that the materials can act as photocatalyst (Pc). The photoactivity of zinc oxide under visible light is well known [21, 24, 35–37]. As expected, the highest porosity of ZnSA led to the best adsorption performance, due to the highest dispersion of the active centers, terminal OH groups on the surface. The acquired results indicate that the terminal OH groups play a crucial role on the extent of adsorption and the degree of CEES transformation.

The absorption of a photon leads to the excitation of the photocatalyst (Pc*):

$$Pc + hv \rightarrow Pc*$$
 (1)

The exited surface of the photocatalyst uses the energy for a primary photocatalytic reaction. Therefore, after being adsorbed (most likely by hydrogen bonds) [38], CEES is transformed into ethyl ethyl sulfonium (EES) cation by means of a photoinduced electron transfer (PET) reaction [29, 39]:

$$Pc * + CEES \rightarrow Pc^{-} + EES^{+}$$
 (2)

It has been reported that once EES^+ is formed, it may be converted to a cyclic cation through an intermolecular cyclization process [29, 40–43]. After that, a labile hydrogen from the cation transfers to the negatively charged lattice oxygen of the zinc phase that acts like a Lewis base [44, 45]. This proceeds via an bimolecular elimination (E2) pathway, resulting in the formation of the dehydrohalogenation vinylic product, EVS [33, 46]. Simultaneously, the chloride anion reacts with a zinc atom on the surface-forming ZnCl₂. Zafrani and co-workers reported that the main degradation product of anhydrous HD on Al₂O₃ was VVS [47]. In our study, EVS was detected on the ZnSA and ZnRA samples only after the CEES exposure at light.

When hydroxyl groups and/or physisorbed water molecules are present, the CEES transformation can proceed by a substitution of the Cl⁻ ion by the OH group [42]. The crucial role of water has been reported for CaO [48]. Absorption of a photon excites the electron from the valence to the conduction band of $Zn(OH)_2$. The formed hole reacts with water associated with the hydroxyl groups in the zinc hydroxide phase, resulting in the formation of hydroxyl radicals [49]. S-CH₂CH₂Cl is destabilized by the electron/hole pair and gets transformed to a transient radical. The latter reacts with the hydroxyl radical that acts as nucleophile, producing the hydrolysis product, HEES [33]. It remains on the surface probably by physical interactions, such as hydrogen bonding. Since water, light, and thus formation of OH radicals are crucial for this process, HEES was formed and detected only on the ZnSA sample exposed to light. Other studies have also shown that the terminal groups participated in photochemical reactions via the formation of hydroxyl radicals, therefore enhancing the removal of sulfide species such as CEES [44] or H₂S [49]. The rate-determining step is the transformation of the cations to HEES, which is enhanced by light [41, 42]. The same pathways were proposed by Martyanov and co-workers on TiO₂ [32], and Singh and co-workers on vanadium oxide [14], where large amounts of water and isolated hydroxyl groups contributed to the formation of HEES. Furthermore, Zafrani reported that on Al₂O₃ in the presence of water HD degraded to thiodiglycol instead of divinyl sulfide [47]. In our study, hydroxyl groups and associated with them water lead to the formation of HEES on ZnSA upon the light exposure. It is worth to mention that the two degradation products obtained on our materials are considerably less toxic than the CWA surrogate used in this study. Based on the results obtained, a schematic representation of reaction pathways on the surface of our materials is proposed (Fig. 5.19).



Fig. 5.19 Proposed reactions scheme of CEES reactive adsorption upon the visible light exposure. (Reprinted from Ref. [1], Copyright 2017, with permission from Elsevier)

5.1.2.9 Conclusions

The results presented in this chapter show that various addition rates of the precipitation agent (NaOH) to a zinc chloride solution results in materials with entirely different physicochemical nature. Slow rates lead to the formation of orthorhombic particles of Zn(OH)₂, while rapid addition forms flower-like ZnO nanoparticles. The former sample compared to the latter showed higher:

- (1) Number of terminal hydroxyl groups by 249%;
- (2) Number of bridging oxygen groups by 27%;
- (3) Surface area by 347%;
- (4) Total pore volume 832%;
- (5) Wider band gap by 6%;
- (6) Weight uptake performance under light exposure by 263%;
- (7) Weight uptake performance in the dark by 120%.

The almost double weight uptakes after CEES exposure measured at ambient light than compared to that in dark on ZnSA reveal photoreactivity. Even with a wider band gap, ZnSA showed significant greater photoreactivity and adsorption performance under light irradiation. The dependences of the adsorption performance on the chemical and structural features showed the terminal hydroxyl groups as the most important. These groups are involved in the hydrolysis reactions, which take place on the surface and thus enhance the detoxification ability of the samples. The surface area was also found to play a crucial role by increasing the dispersion of the active sites and thus their contact with the organic molecules.

Ethyl vinyl sulfide was identified as the main degradation products for all materials when the adsorption tests were performed in the light. In the case of ZnSA, the detected concentration of EVS was the highest and hydroxyethyl ethyl sulfide (HEES) was also detected at the extracts. This supports the enhanced photoactivity of ZnSA. The degradation of CEES is triggered by the excitation by photons, which promote the formation of the intermediate cyclic ethyl ethyl sulfide cation and the formation of OH radicals. When the adsorption tests were performed in dark, the detected amount of EVS was dramatically lower and no HEES was detected at the extracts.

5.1.3 Effect of GO Phase in Zn(OH)₂/GO Composites on the Extent of Photocatalytic Reactive Adsorption

5.1.3.1 Introduction and Materials

The objective of this study was the evaluation of effects of GO addition on the structural and chemical features of the adsorbents and on the extent of reactive adsorption. An additional objective was to identify the optimal amount of GO which could lead to an improvement in their performance as adsorbents and catalysts. Pure zinc hydroxide is referred to as ZnOH and the composites—as ZnGO1, ZnGO5, ZnG10, and ZnGO20, where the numbers represent the wt/wt% of GO to the final mass of the material. Finally, since 24 h of exposure was arbitrarily chosen, the exposure time of the adsorption tests was extended until the maximum weight uptake was obtained for each sample. All the adsorption tests were carried out at ambient conditions.

5.1.3.2 Structural and Morphological Characterizations

In order to determine whether or not the addition of GO altered the formation of the zinc hydroxide structure, the synthesized composites were analyzed by powder XRD (Fig. 5.20). The diffractograms of ZnOH showed zinc hydroxide as a predominant crystallographic phase. Traces of zinc oxide were also present. This results in agreement with the X-ray diffractograms in the previous sub-chapter,



Fig. 5.20 X-ray diffraction patterns for GO and the initial samples. (Reprinted from Ref. [2], Copyright 2017, with permission from Elsevier)

although different batches of the materials were used in this study. Interestingly, the diffractograms of the composites clearly indicate that the only crystallographic phase is ε -Zn(OH)₂, since no diffractions related to ZnO or impurities were detected. The diffraction peaks can be indexed as those of orthorhombic wülfingite (JCPDS 38-0385) [5]. The absence of the characteristic peak corresponding to the d₀₀₂ of GO at around 10.2 20 suggests its exfoliation during the composite formation. The average crystallite size for all the materials was calculated from the (101) diffraction using the Scherrer equation. For ZnOH, the average crystallite size was estimated to be about 49.2 nm, while for the composites, the values of 35, 39, and 43 nm for 5, 10, and 20% of GO, respectively, were found.

 ϵ -Zn(OH)₂ particles with bipyramid shape of micrometric size are visible on the SEM image of ZnOH (Fig. 5.21a). Limited amount of zinc oxide particles can be also seen with a platelets-like shape of a micron range size. The particle morphology dramatically changed upon the addition of GO, especially for the composites with the higher amount of GO. In ZnGO5, bipyramid particles of several tens of nanometers, linked to the Zn(OH)₂ phase (Fig. 5.21b), surround the graphite oxide sheets, forming a web-like network with a high level of surface roughness [16, 49]. A further increase in the amount of GO results in a higher dispersion of the inorganic phases around the GO sheets, and the bipyramid particles are not detectable for both ZnGO10 and ZnGO20.



Fig. 5.21 SEM images of ZnOH (a), ZnGO5 (b), and ZnGO10 (c). (Reprinted from Ref. [2], Copyright 2017, with permission from Elsevier)

Since it was shown previously that the porosity and the surface area are key factors for the performance of adsorbents, especially for physical adsorption, nitrogen adsorption isotherms were measured on all samples. The parameters of the porous structure calculated from these isotherms are summarized in Fig. 5.22. The synthesis approach used led to composites with improved surface areas and total pore volumes, and marked structural heterogeneity. Compared to ZnOH, ZnGO5 showed a slight decrease by 4 and 21% in the surface area and total pore volume, respectively. The highest values of the porous structure parameters were obtained for ZnGO10. The surface area increased by 43%, while the total pore volume showed an even higher increase (67%) as compared to the corresponding structural parameters of ZnOH. Further increase in the amount of GO resulted in a decreased porosity. This can be linked to limitations in the spatial growth of the zinc hydroxide phase. It appears that 10% of GO is the optimal amount, resulting in the most pronounced porosity.

5.1.3.3 Surface Chemistry Analysis

The surface chemistry of the samples was analyzed by potentiometric titration (Fig. 5.23). The addition of 5% GO slightly altered the amount and the distribution of the surface oxygen-containing groups. On the other hand, a higher amount of GO led to a marked increase in the amount of the terminal hydroxyl groups, while the bridging groups showed a dramatically decrease. ZnGO10 was found to have the highest amount of terminal groups (22% increase compared to ZnOH), while it revealed a 79% decrease in the amount of bridging groups. ZnGO20 showed a less



Fig. 5.22 Parameters of porous structure calculated from the nitrogen adsorption isotherms. (Reprinted from Ref. [2], Copyright 2017, with permission from Elsevier)



Fig. 5.23 Amounts of terminal and bridging oxygen-containing groups detected from potentiometric titration experiments. (Reprinted from Ref. [2], Copyright 2017, with permission from Elsevier)

pronounced increase in the amount of the terminal hydroxyl groups and almost equal amount of bridging groups, compared to ZnGO10.

The ratios of the terminal to bridging groups are 0.8, 1.4, 5.0, and 5.6 for ZnOH, ZnGO5, ZnGO10, and ZnGO20, respectively. It can be seen that the addition of the carbonaceous phase led to an increase in the dispersion and amorphicity level of zinc hydroxide, since 10 and 20% of GO resulted in the highest ratios of terminal to bridging groups.

5.1.3.4 Adsorption Performance and the Optimum Amount of GO

The reactive adsorption was expected to be affected by the altered textural and chemical surface features. The first goal was to determine whether the addition of the carbonaceous phase led to an improvement in the weight uptakes after 24 h. The tests were carried out in ambient light (L1) and under a solar light simulator (SL1) in order to evaluate the role of the light intensity. For comparison, the tests were also performed in dark. The capacities expressed in weight uptake (mg) per gram of the adsorbents are collected in Fig. 5.24.

Interestingly, no difference between the two different light sources was detected, suggesting that the density of the irradiation does not play a role. Further qualitative trials with different light densities from the solar simulator were held, in order to double check whether the light irradiation density could change the adsorption performance. In all cases, no differences were observed. The fact that all samples



Fig. 5.24 Capacities measured after 24 h at various conditions exposure (ambient visible light, solar light simulator, in the dark)

the weight uptakes in dark were almost twice smaller than those measured at light indicates that the composites are photoactive even under ambient light. Moreover, the better adsorption performance in visible light than in dark indicates the relevant role of light in improving the adsorption of CEES and/or its degradation products on the surface. This effect is found to be more pronounced for the composites than for $Zn(OH)_2$.

The addition of the carbonaceous phase led to bigger weight gains after the one-day exposure for all composites compared to that on ZnOH, either at light or in dark. It is worth to mention at this point that for GO, the weight uptakes under all conditions were negligible. The weight uptake on ZnGO10 was the highest one under ambient light (81% higher than that on ZnOH). This increase was less pronounced in dark (+49%). On ZnGO5, the least effect of GO on adsorptive performance was found (27% at light and 9% in the dark compared to ZnOH). On the other hand, the weight uptake on ZnGO20 was significantly higher compared to that on ZnOH, but compared to ZnGO10, the capacities were lesser by 22% under ambient light and 17% in the dark. The results confirmed that the optimal amount of GO in the composites that led to the maximum decontamination performance was 10% w/w of the final composite mass.

5.1.3.5 Role of the Textural Parameters

In order to elucidate the role of the porosity of our materials in the reactive adsorption process, the dependence between the weight uptake and the surface areas (S_{BET}) or

total pore volume was analyzed (Fig. 5.25). The surface area found to play a role when the sample was exposed to CEES in dark, since the obtained correlation coefficients is 0.93. This suggests that in dark, the CEES molecules are mainly retain on the surface via physical adsorption and the degradation is limited. On the other hand, no correlation was found in the case of the light irradiation. This suggests that the presence of light promotes alternative adsorption/degradation pathways. No correlation between the capacity and the total pore volume could be established.

5.1.3.6 Role of the Surface Chemistry

The dependence between the weight uptake and the number of the terminal –OH groups (S_{BET}) or bridging groups showed a linear trend, with correlation coefficients 0.99 and 0.94, respectively (Fig. 5.26). The stronger correlation in visible light designates the key role of the hydroxyl groups in the photoactivity of these samples. No correlation was found between the weight uptake and the amount of the bridging groups. ZnGO10 showed the largest surface area and the highest number of terminal hydroxyl groups. Those two factors certainly play crucial roles enhancing the CEES adsorption performance of this material and can be considered as linked to each other since a developed surface area promotes a favorable dispersion of the reactive adsorption centers/terminal OH groups.

5.1.3.7 Study of the Kinetics and the Maximum Detoxification Performance

We cannot cross out the probability that slow reactions of CEES and the products formed on the surface of the adsorbents are taking place for longer time than 24 h,



Fig. 5.25 Dependence of the amount adsorbed (after 24 h) on the surface area (a) and the total pore volume (b) under light exposure and in the dark



Fig. 5.26 Dependence of the amount adsorbed (after 24 h) on the number of the terminal OH groups (a) and the bridging groups (b) ate light exposure and in the dark

since this duration was arbitrary chosen for the adsorption/reaction process. Moreover, the materials can act as photocatalyst, degrading adsorbed CEES. For those reason, the adsorption tests were carried out for up to nine days, in order to examine the extent of the processes governed by the kinetics of the adsorption and degradation performance. The increase in the weight of the samples exposed for various periods of time (up to 9 days) was recorded. These tests were carried out at ambient light irradiation, due to the fact that the usage of the solar light simulator did not alter the adsorption uptake. The further discussion focuses on ZnOH and ZnGO10, since the latter was the best-performing composite, and ZnOH was chosen for the sake of the comparison.

The recorded weight uptakes are collected in Fig. 5.27. Interestingly, the weight gain continues until the eighth day for both samples. The dependence of the capacity on the exposure time up to the sixth day shows a linear trend with correlation coefficients 0.998 for ZnGO10 and 0.991 for ZnOH. The weight gained on day 7 reached almost equal value to the initial mass of the samples (20 mg). This indicates that more than the half of the volume of the initially injected CEES transferred to the adsorbents' surfaces. Until the sixth day, the uptake on the composite was higher than that on ZnOH. This can be due to the higher dispersion of the active sites promoting the higher degradation reactivity.

The capacities until the sixth day were fitted to the linearized-integral form of the Lagergren's pseudo-first-order kinetic model. The plot of $ln(q_e-q_t)$ against time (q_e is the maximum recorded capacity and q_t is the amount adsorbed at the specific time) revealed a linearity with high correlation coefficient R² (0.981 for ZnGO10 and 0.968 for ZnOH). The pseudo-first-order model [50] indicates that the adsorption rate is constant and not affected by the amount of the material.



Fig. 5.27 Weight gains measured at visible light for up to nine days. The change in the slopes of lines indicates the change in the chemistry/physics of the interface (condensation of adsorbents on the surface and saturation). (Reprinted from Ref. [2], Copyright 2017, with permission from Elsevier)

The weight uptake on zinc hydroxide overcame the one of the composites after seven days of interactions. A liquid film formed on the surface of the ZnOH sample, which can be linked to the condensation of CEES or of the products of its reactive adsorption. The color of the material changed from white to yellowish. Additionally, the sample began to resemble rather a gel than a solid matter and the weight was gained at a higher rate. The latter stopped with the saturation of the sample with condensed vapors (no change in weight recorded) on the ninth day. This condensation might be responsible for a change in the reactivity since the liquid layer on the surface of the sample will change the nature of interactions. The adsorption rates indicate that the samples are acting as catalyst until they get saturated with reactants. In the case of ZnGO10, the time needed to reach the saturation is longer than that for ZnOH and the condensation of vapors starts after the eighth day. That delay in the surface condensation might be related to a higher catalytic activity, the improved porosity, and/or higher number of terminal hydroxyl groups of the composite than those of ZnOH.

It is worth to mention that the maximum weight uptakes recorded on the ninth day were 1339 and 1236 mg per gram for ZnOH and ZnGO10, respectively. The amounts adsorbed on the surface of ZnOH and ZnGO10 represent 63 and 58% of the total initial volume of initially injected CEES, respectively. If the entire injected CEES were totally evaporated, the maximum possible capacity would be 2120 mg/g (by assuming that the entire amount of the CEES retained on the surface). Since no liquid CEES

remained in the vessel, the difference of the theoretical maximum capacity and the recorded suggests that unreacted CEES or its degradation products remained in the headspace.

5.1.3.8 Surface Chemistry Analysis of the Exhausted Samples

FTIR spectra of the initial and the exhausted samples were analyzed (Fig. 5.28), in order to determine the species deposited on the surface after the exposure. A comparison of the spectra for the initial ZnOH and ZnGO as well as for the exhausted samples exposed to CEES for 7 days in light is collected in Fig. 4.3.9. In the spectrum of initial ZnOH, the bands at 715 and 900 cm⁻¹ are linked to the out-of-plane bending and vibration modes of the OH groups, while the bands



Fig. 5.28 FTIR spectra for the initial and exhausted ZnOH and composite samples after day 7 of CEES exposure (L7). (Reprinted from Ref. [2], Copyright 2017, with permission from Elsevier)
observed at 830, 1040, and 1090 cm⁻¹ are assigned to the deformation vibration of -OH groups, Zn–OH bending, and -OH twisting vibration, respectively. The bands at 1390 cm⁻¹ with a shoulder at 1360 cm⁻¹, and at 3450 cm⁻¹ are assigned to the vibrations of OH groups coordinated to Zn(II) ions, while the bands at 1500 and at 3240 cm⁻¹—to the hydroxyl groups of water. Similar bands as those for ZnOH are visible on the spectrum of ZnGO, but with a lower intensity of the out-of-planes bending and vibration modes of the hydroxyl groups. The weak bands in the region between 620 and 660 cm⁻¹ are linked to the vibrations of C–C and C–H bonds of the epoxy and carboxylic groups of graphite oxide (GO) were not detected [51, 52]. This supports that these oxygen functionalities were involved in the formation of the bonds with the inorganic phase.

For the exhausted samples, groups of new bands appeared in various regions of the spectra. A summary of the formed products and the vibrational frequencies used to monitor these products is given in detail in Table 5.2. For the exhausted samples, the spectral regions below 1720 cm⁻¹ contain a complex overlap of stretching and deformation vibrational modes of aliphatic CH_x, alone or bonded to heteroatoms (chloride or sulfur). The characteristic bands at 2976, 2886, 1453, and 1267 cm⁻¹ can be assigned to $-CH_2Cl$, as a result of adsorbed CEES molecules on the surface [33]. The characteristic bands from the stretching vibrations of C=C and C–H bonds of the monosubstituted alkenes (at 2976, 1613, 1550, 1593, and 900 cm⁻¹) from the vinyl group (C=CH₂) [53] indicate the presence of dehydrohalogenation vinylic products such as ethyl vinyl sulfide (EVS), vinyl vinyl sulfide (VVS), and methyl vinyl sulfide (MVS). The bands at 900 and 715 cm⁻¹ show a significant intensity increase and are linked to the vibrations of the disubstituted C–H.

A dramatically increase in the intensity of the band located between 3600 and 3200 cm^{-1} for the exhausted samples is revealed. This broad band is attributed to the hydroxyl-stretching mode [54] and can be assigned either to the formation of

Freq. (cm ⁻¹)	Vibration mode	Assignment	References
3450	v(O-H)	(-CH ₂ OH)	[38, 58]
2976	v(CH ₂) _{as} , v(CH ₂ Cl) _{as} ,	(C ₂ H ₃), (CH ₂ Cl)	[33, 58]
2932	$v(CH_3)_{as}, v(CH_2S)_{as},$	-(C ₂ H ₄), (-CH ₂ S)	[33, 58]
2886	v(CH ₂) _s , v(CH ₂ Cl) _s , v(CH ₂ S) _s ,	(-CH ₂ S), (-CH ₂ Cl)	[33, 58]
1613	v(C=C)	(CH=CH2)	[53, 59]
1453	$\delta(CH_3)_{as}$ bend, $\delta(CH_2)_s$	(-S-CH ₃)	[33, 46, 58]
1422	$\delta(CH_2)_{as}$ scissor	(CH ₂ S-) or (C ₂ H ₃)	[33, 58]
1383	$\delta(CH_3)_s$ bend	(-S-CH ₃)	[33, 58]
1267	$\delta(CH_2Cl)_{wag}, \delta(OH)^b$	(-CH ₂ Cl), (-CH ₂ OH)	[33, 58]
1215	δ(CH ₂ S) _{wag}	(CH ₂ S-)	[33]
970	δ(CH ₂) _{wag}	(=C-H)	[33]

Table 5.2 Assignment of bands detected on FTIR spectra of ZnOH and ZnGO10 exposed to CEES $% \left(\mathcal{A}_{n}^{\prime}\right) =\left(\mathcal{A}_{n}^{\prime}\right) \left(\mathcal{A}$

2-hydroxy ethyl ethyl sulfide (HEES), H₂O, or also associated with the hydrogen-bonded molecules to the Zn–OH groups on the surface. Both chlorine and sulfur atoms can act as potential hydrogen-bond acceptor sites. Similar spectral changes, due to the hydrogen-bonded molecules, have been reported for the photocatalytic oxidation of CEES on TiO₂ [55]. Moreover, the bands at 1422 and 1267 cm⁻¹ can be attributed to the deformation vibrations of the –OH in the – CH₂OH group [33, 56, 57]. The absence of bands related to the stretching vibration of C=O at the region of aldehydes and ketones (1780–1650 cm⁻¹) indicates that no carboxylic acids, esters, or ketones were formed on the surface [33, 56, 57]. The distinguishable bands related to sulfate groups were also not detected. In summary, the analysis of the FTIR spectra for the exhausted samples revealed that CEES, HEES, and vinylic products exist on the surface.

5.1.3.9 Identification of the Retained on the Surface Reaction Products

Thermal analysis and MS-MS analysis of the extracts were used to further evaluate the nature of the degradation products formed during the surface interaction reactions. At this stage, it is considered helpful, for the sake of discussion, to introduce the characteristic mass-to-charge ratios (m/z), based on them was held the identification of the compounds. The names of the detected compounds on the surface and in the headspace, along with their nomenclature, chemical formulas, abbreviations, and the method used for their detection, are listed in Table 5.3

Thermal gravimetric (TA) and differential thermal gravimetric (DTG) curves measured in helium atmosphere are collected in Fig. 5.29. For initial ZnOH, the DTG curve was analyzed in the previous sub-chapter. For ZnGO, the intense peak on the DTG curve between 130 and 170 °C can be assigned to the removal of the

Name	Linear formula	Abbrev.	Identification based on	Characteristic mass-to-charge ratio (m/z)
2-chloroethyl ethyl sulfide	CH ₃ CH ₂ SCH ₂ CH ₂ Cl	CEES	TA-MS, GC-MS, MS-MS	124, 109, 89, 75, 61, 47
Ethyl vinyl sulfide	CH ₃ CH ₂ SCH=CH ₂	EVS	TA-MS, GC-MS, MS-MS	88, 73, 60, 59, 45
2-hydroxyethyl ethyl sulfide	CH ₃ CH ₂ SCH ₂ CH ₂ OH	HEES	TA-MS, MS-MS	106, 75, 61, 47
Vinyl vinyl sulfide	CH ₂ =CHSCH=CH ₂	VVS	TA-MS, GC-MS	86, 85, 71, 59, 41, 40
Methyl vinyl sulfide	CH ₂ =CHSCH ₃	MVS	TA-MS, GC-MS	74, 59, 47, 44, 40

Table 5.3 Details on the detected compounds on the surface and in the headspace. (Reprinted from Ref. [161], Copyright 2017, with permission from Elsevier)



Fig. 5.29 TA and DTG curves for the initial, after 1-day (L1) and after 7-day (L7) exposure to CEES vapors in visible light for ZnOH and ZnGO10. (Reprinted from Ref. [2], Copyright 2017, with permission from Elsevier)

physically adsorbed or structural water molecules, while the peak assigned to the dehydration of $Zn(OH)_2$ phase centered at 215 °C is overlapped from the intense peak of the GO decomposition. The shoulder at about 450 °C can be attributed to the totally dehydroxylation of $Zn(OH)_2$ [60]. The additional wide peak over 800 °C is assigned to the reduction of formed zinc oxide to Zn (boiling point 907 °C) [30] by the carbonaceous phase.

For both exhausted samples after 7-day CEES vaporexposure, the enlarged weight loss up to 170 °C is related to theremoval of water molecules and to the large amount of the degradationproducts of lower boiling points than that of CEES, such as MVS (b.p.86 °C), VVS (b.p. 78–92 °C) and EVS (b.p. 92–97 °C) [30]. Physically adsorbed CEES andHEES with boiling points of 156 and 184 °C [30], respectively, were removed from the pores at the temperature range around 210 °C. Moreover, the new peak that appears for both samples at 460 °C can be assigned to the decomposition of the new surface products such as ZnCl₂, ZnS, and ZnSO₄ [60]. The existence of new sulfur-containing products can be supported by the color change of the samples after the thermal analysis. The exhausted ZnGO sample after 7-day exposure was gray before the TA analysis, but it turned to yellow afterward (Fig. 5.30). ZnOH L7 was bright white before the thermal analysis, and it turned to yellowish. In the case of the latter sample, it can be observed the marked mass loss after the thermal analysis (Fig. 5.30c, d).

To further analyze the compounds formed as a result of the interactions/ decomposition during the exposure to CEES and retained on the surface, the



Fig. 5.30 Exhausted ZnGO10 L7 composite before TA analysis (a) and afterward (b). For comparison, the exhausted ZnOH L7 before (c) and after TA analysis (d). (Reprinted from Ref. [2], Copyright 2017, with permission from Elsevier)

extracts from the exhausted samples were tested by MS-MS. The compounds detected on both samples were EVS, HEES, and CEES. No traces of VVS, MVS, or any oxidation product (diethyl sulfoxide, diethyl sulfone, or diethyl sulfone) were found. This does not exclude the presence of the latters in the headspace in a non-adsorbed form.

5.1.3.10 Identification of the Volatile Products in the Headspace

Although the weight uptakes and the detailed analysis of the exhausted samples are important for assist the evaluation the adsorption performance in solitary, they cannot deliver enough information to totally understand the photocatalytic activities. The results presented above suggest that the adsorption process includes photodegradation of CEES vapors simultaneous with chemical and/or physical adsorption of various formed compounds and no degraded CEES. It is possible that the many products formed during the adsorption process do not remain on the surface, especially if they are of high volatility.

Consequently, the analysis of the headspace provides additional information, which helps to determine the reactive adsorption pathways. The qualitative and semiquantitate identification of the volatile compounds in the headspace was carried out using GC-MS.

The analysis of the chromatograms indicated that the amount of CEES in the headspace of the closed reaction vessel gradually decreased with the exposure time. Except CEES, the compounds detected were EVS, VVS, and MVS. Interestingly, the latter two compounds were not detected at the acetonitrile extracts from the surface. The comparison of the chromatograms of ZnGO10 and ZnOH after 6 days of exposure is shown in Fig. 5.31. Only the chromatograms after 6 days of adsorption are presented, since, as it was aforementioned, after 7-day vapors started to condense on the surface of ZnOH. For the composite, the intensity of the peaks related to the photodegradation of CEES was higher, while the peak of unreacted CEES had lower intensity (retention time 5.1 min). Similar trend was found for the samples exposed to CEES for all time periods. The revealed enhanced photocatalytic performance of the composite can be attributed to the alteration in the surface.



Fig. 5.31 Chromatograms of the headspace for ZnOH and ZnGO10 after 6 days of CEES exposure. (Reprinted from Ref. [2], Copyright 2017, with permission from Elsevier)

and chemical heterogeneity as a result of the GO addition. The developed porosity as well as the increased amount and the higher dispersion of the hydroxyl groups play a key role.

The analysis of the chromatograms suggests that the degradation of CEES undergoes mainly through the dehydrohalogenation, since the most intense peak is the one of EVS. This is in a good agreement with the results obtained from the analysis of the extracts by MS-MS. The absence of HEES in the headspace could be due to its high boiling point (180–184 °C) and/or the possibility to form hydrogen bonds with surface sites. This might result in its strong retention on the surface.

The adsorption progress in the case of ZnGO10 was monitored analyzing the evolution of the chromatograms features and the peak areas of every detected compound in the headspace for up to nine days, as in Figs. 5.32 and 5.33, respectively. After a day, only the peak related to CEES was visible. The absence of other peaks indicates that the formed products remained adsorbed on the surface and/or in the pores of the absorbents. In fact, EVS and HEES were detected in the extracts of after 1-day exhausted sample. The continuous photocatalytic transformations of CEES until the sixth day can be clearly observed from the gradually decreasing intensity of the CEES' signal and the increase of the EVS, VVS, and MVS signals. After the sixth day, the decreasing trend of the intensity of the peaks linked to the formed degradation products can be due to the vapor condensation on the surface of the sample. This supports further the conclusion that the sample is acting as a photocatalyst, until its surface get saturated with CEES and/or with the formed compounds.

It is important to mention that after eight days, the liquid CEES totally evaporated from the container in the reaction vessel of ZnGO10, while after nine days of exposure, no CEES was detected in the headspace. These two facts indicate that the entire initially injected amount of CEES either retained on the surface of the samples or degraded.



Fig. 5.32 Tracking of the progress of adsorption and reactions by monitoring the chromatograms of ZnGO10 for up to 9 days. (Reprinted from Ref. [2], Copyright 2017, with permission from Elsevier)

Taking into account the maximum weight uptake of the exhausted ZnGO10 (1236 mg/g) and the density of CEES ($d_{CEES} = 1.06$ g/mL), the amount of the surrogate that retained or decomposed on the surface after 9 days was 58 wt%. Thus, the remaining 42% was totally degraded. Remarkably, our composite has the ability for detoxification of the amount of CEES that exceeds twice of its mass. On the other hand, ZnOH did not detoxify the entire CEES, since at the headspace after 9 days of exposure, CEES was still detected, while the liquid CEES did not get totally evaporated. Even though the weight increase of ZnOH was higher than that on ZnGO10, its performance for vapor detoxification was less pronounced. It is possible that the major factor affecting this performance is the condensation of CEES on the surface, limiting the interactions of the surface active sites with the vapors. The adsorption test was carried out also on the pure GO under light or in the



Fig. 5.33 Dependence of the area of the chromatographic peak (analysis of the headspace) for the particular compounds on the exposure time for ZnGO10. (Reprinted from Ref. [2], Copyright 2017, with permission from Elsevier)

dark for up to nine days. The analysis of the headspace and the extracts from the exhausted materials did not reveal any formation of the degradation products.

5.1.3.11 Detoxification and Adsorption Mechanisms

The degradation pathways of CEES to the less toxic EVS and HEES on $Zn(OH)_2$ and ZnO for 24 h of exposure have been thoroughly reviewed and analyzed in the previous sub-chapter. Briefly, the detoxification to the dehydrohalogenation vinylic product, EVS, takes place via a bimolecular elimination (E2) pathway. Adsorbed CEES is transformed to ethyl ethyl sulfonium cation. Then, through an intermolecular cyclization process, it is converted to a transient intermediate cyclic cation. Negatively charged lattice oxygen of the zinc hydroxide phase acts like a Lewis base and accepts labile hydrogen from the cation. Simultaneously, a Zn atom reacts with the produced Cl^- to form zinc chloride. This pathway is promoted by photoexcitation of the material. By the absorption of a photon, an electron is excited from the valence to the conduction band of the zinc hydroxide phase, resulting in the formation of an electron–hole pair. The formed electron/hole pair leads to the



Fig. 5.34 Schematic representation of the radical reactions. (Reprinted from Ref. [2], Copyright 2017, with permission from Elsevier)

formation of hydroxyl radicals [32] and simultaneously the formation of a transient radical from the destabilization of CEES. This transient radical can react with a hydroxyl radical, forming HEES, or it can get involved in the cleavage of a C–S and/or a C–C bond. Transient radicals can be also formed from the destabilization of the formed EVS.

The distinctive finding at the reactive adsorption of CEES on our composites, except the total detoxification of the CEES vapors in a closed system, is the detection of MVS and VVS in the headspace. The formation of these compounds is promoted by the high photoreactivity of the surface, which promotes additional radicals' reaction of the produced EVS. The surface of the composite exhibits a high efficiency for the photodecomposition of CEES, and GO seems to increase the efficiency of electrons transfer owing to its electrical conductivity.

The contribution of the radical reactions to the catalytic formation of VVS, MVS, EVS, and HEES deserves more attention. The photogenerated holes in the valence band and the photogenerated electrons at the conduction band and the hydroxyl radicals play a crucial role in the photochemical destruction of CEES, by attacking the formed EVS, following the reactions schematically shown in Fig. 5.34 (1, 2, and 3). The presence of water during the adsorption is a constant source of hydroxyl anions that are transformed to hydroxyl radicals when reacting with the

formed holes (Fig. 5.34, reaction 8). It is also possible that H_2O condenses on the surface, forming an ultra-thin layer with an increased radical population. This can be explained by the observed gel-like state of the absorbents after eight days of exposure in the case of ZnGO10 and after seven days for ZnOH. Moreover, the water formation on the surface can be confirmed by the intense bands on the FTIR spectra of the exhausted materials (Fig. 5.28), as well as by the marked weight loss observed at the temperature less than 100 °C during the thermal analysis of the exhausted samples (Fig. 5.29).

The thiol radical (EVS) can undergo further elimination to form VVS by the creation of a vinylic bond (Fig. 5.34, reaction 4) or to form MVS through the cleavage of the C–C bond (Fig. 5.34, reaction 5). The "fishhook" half arrows indicate the transfer of a single electron. The formation of EVS can also happen through an intermolecular radical pathway of the produced ethyl ethyl sulfide radical from the adsorption of a photoexited electron (Fig. 5.34, reaction 6). It was previously reported that sulfides may undergo the cleavage of S–C bonds (two in CEES molecule), resulting in various radicals [58]. These radicals can recombine forming disulfides, which are toxic, but less than is HD. This pathway was reported in the case of the photocatalytic oxidation of CEES on TiO₂ [32]. Disulfides were not detected on the surface or at the headspace of our samples by any of the analytical techniques.

Based on the obtained results, a collective schematic representation of all the reaction pathways is proposed in Fig. 5.35. Since in our vials-in-vial adsorption system the surrogate does not directly interact as a liquid with a solid, the first step is its evaporation (Fig. 5.35, I). CEES vapors in an adsorbed state interact then on the surface of our absorbents (Fig. 5.36, II). How fast the equilibrium is reached in Step I and Step II plays a crucial role in the reactive adsorption process. It is proposed that the adsorbed CEES undergoes the above-mentioned photocatalytic reactions pathways, which lead four degradation products (EVS, HEES, MVS, and VVS), which are less toxic compared to CEES or non-toxic.



Fig. 5.35 Schematic representation of all interactions inside the closed adsorption vessel. (Reprinted from Ref. [2], Copyright 2017, with permission from Elsevier)



Fig. 5.36 X-ray diffraction patterns for the initial samples

5.1.3.12 Conclusions

The successful formation of the composite of zinc hydroxide and graphite oxide resulted in an improved detoxification performance compared to pristine zinc hydroxide, since both adsorption and photocatalytic degradation ability of the materials remarkably increased. The synergistic effect of the formation of a composite led to a development of the most important features governing the detoxification performance, such as surface area, total pore volume, and number of terminal hydroxyl groups. The extent of surface features alterations, as well as the adsorption performances, strongly depend on the amount of the carbonaceous phase in the composite. The addition of GO has a positive effect on:

- (1) surface structural and chemical heterogeneity;
- (2) dispersion of the inorganic phase;
- (3) number of terminal –OH groups;
- (4) surface area and the total pore volume;
- (5) efficiency of electron transfer/separate holes from electrons;
- (6) adsorption capacity;
- (7) degradation-detoxification yield.

The optimal amount of GO was found to be 10%. The significantly higher weight uptakes in visible light compared to those measured in dark confirm the existence of the photocatalytic reactivity. The comparison of the composites, which consists of 10 percent of GO to the pure zinc hydroxide, showed the following numerical increases, compared to $Zn(OH)_2$:

- (1) Number of terminal hydroxyl groups by 22%;
- (2) Surface area by 43%;

- (3) Total pore volume by 67%;
- (4) Weight uptake performance after 24 h of exposure under light irradiation by 81%;
- (5) Weight uptake performance after 24 h of exposure in dark by 49%.

The increased density of the hydroxyl groups and chemical heterogeneity (presence of the carbon based phase) in the composite promoted the dispersive interactions of the organic molecules with the active sites of the adsorbents. Moreover, the active radicals on the composite with 10% of graphite oxide are formed with greater efficiency than on $Zn(OH)_2$. The sample retained and/or decomposed the entire amount of CEES introduced to the system, which exceeds more than twice the mass of the composite, after nine days of exposure. This improved photocatalytic detoxification ability is a desirable property. Finally, the formed products are less toxic or non-toxic, which is an important feature of an effective decontamination process.

5.1.4 AuNPs and AgNPs Embedded in Nanostructured Composites of Zinc (Hydr)Oxide/GO

5.1.4.1 Materials and Objectives

The next goal was to evaluate whether an addition of gold or silver nanoparticles can further promote the adsorption and photocatalytic degradation of CEES, under visible light irradiation. For that reason, the composites with zinc hydroxide, graphite oxide, and NPs were synthesized, following the same synthetic procedure of the zinc hydroxide/GO composite. The arbitrarily chosen amount of NPs was 1 wt/ wt% of the final total mass and 10% of graphite oxide, since this amount of GO was found previously to be the optimal. The composite of zinc (hydr)oxide, GO, and AuNPs is referred to as AuZnGO, while the sample with AgNPs is referred to as AgZnGO. ZnGO was used in the analysis of the data for the sake of comparison.

5.1.4.2 Structural and Morphological Characterizations

The X-ray diffraction patterns of ZnGO, AuZnGO, and AgZnGO samples showed entirely different crystal morphologies (Fig. 5.35). In the case of ZnGO, the diffraction peaks are matching perfectly with those of orthorhombic ε -Zn(OH)₂ (JCPDS 38-0385). [5] The addition of the silver nanoparticles led to the formation of two crystallographic phases. The diffraction peaks at 20.2°, 20.8°, 27.3°, 27.8°, 32.8°, 39.4°, 40.7°, 42.2°, 52.3°, 57.9°, 59.5°, and 60.4° can be indexed as those of orthorhombic ε -Zn(OH)₂, while the diffraction peaks at 31.7°, 34.4°, 36.2°, and 47.6° can be linked to a well-crystallized hexagonal wurtzite structure of ZnO (JCPDS 36-1451) [61]. Low temperature and basicity, during the precipitation without any additive (GO or NPs), facilitate the nucleation and growth of $Zn(OH)_2$ rather than of ZnO [62]. The initial precipitation rate of $Zn(OH)_2$ is faster than that of ZnO, due to the solubility differences [7]. No change to the pH values was observed by the addition of GO and AgNPs, so the resulted formation of the zinc oxide phase can be linked to a different crystallization pathway. The addition of AuNPs led to an entirely altered crystallization process and nucleation mechanism. The XRD diffraction pattern of AuZnGO indicates a high level of amorphicity. The absence of well-defined diffraction peaks can be also attributed to an ultra-small size of the crystals [63].

The SEM images of the samples are collected in Fig. 5.37. The texture of ZnGO (Fig. 5.37a) resembles those previously reported [31, 49]. The carboxylic groups at the edges of GO layers are likely "seeds" for the creation of a web-like network, with the inorganic phase connected to GO particles [31, 49, 60]. The



Fig. 5.37 SEM images of ZnGO (a), AuZnGO (b, c) and AgZnGO (d, f)

orthorhombic-shaped Zn(OH)₂ particles are well crystallized around the organic phase. The composites revealed entirely different structural and morphological features. For the composites consisted of AuNPs (Fig. 5.37b, c), spherical-like particles with sizes between 40 and 80 nm are well dispersed around the graphitic layers, resulting in a highly heterogeneous and amorphous material. The nanoscale crystal size might be responsible for the absence of diffractions peaks at the X-Ray diffractograms. For the composites consisted of AgNPs (Fig. 5.37d, f), both Zn (OH)₂ and ZnO phases can be clearly seen around the GO phase. The zinc hydroxide phase can be detected as orthorhombic-shaped particles, while the zinc oxide as a cobweb-like network. The pore in the shape of cages and tunnels is shown in Fig. 5.37f with sizes from 20 to 500 nm. These pores can promote the diffusion of vapors into the mesopores, which as showed in the previous sub-chapter play the uppermost role on the adsorption performance.

Apparently, an addition of NPs during the composite altered the chemistry of composite formation. The XRD and SEM results showed that in the case of AuZnGO, amorphous nanocrystallites are formed and they homogeneously surround the GO sheets [16]. It has also been previously reported that the presence of metal NPs altered the ZnO growth [64]. It is possible that AuNPs increase the number of nucleation centers for ZnO instead those for $Zn(OH)_2$. This leads to a drop in the size of the particles, which was also reported for alumina [9]. The above-mentioned details of the composite formation with embedded NPs are illustrated in Fig. 5.38.

The sizes of the Ag or Au nanoparticles were estimated by TEM (Fig. 5.39). For the AgZnGO, the spherical shape of AgNPs retained with sizes in the range from 30 to 90 nm. These sizes are in good agreement with the size distribution of the initial AgNPs (see Chap. 3). The AuNPs had even smaller sizes, starting from 10 up to 40 nm. For both AuZnGO and AgZnGO, the NPs were predominantly aggregated on the outer phase of the composites. The high-resolution TEM images of both samples revealed areas with various overlapped lattices. The areas with darker contrast



Fig. 5.38 Proposed mechanism of the AuZnGO and AgZnGO formation



Fig. 5.39 TEM and HRTEM images for the AgZnGO and AuZnGO composites

represent Au⁰ and Ag⁰ nanoparticles, respectively, due to the stronger scattering factor for electrons of these heavier atoms. The predominant gray areas are linked to the iron zinc hydroxide phase, while the even lighter gray areas to the GO phase.

The N₂ adsorption (Fig. 5.40) is of Type II(b) for all composites (according to the extended IUPAC classification) [12] with capillary condensation in inter-particle slits within the aggregates. The absence of a curvature at low p/p^0 indicates the lack of micropores. A very small Type H3 hysteresis loop between the adsorption and desorption isotherms indicates that the pores do not have a complex structure [12]. The hysteresis loop increases for AuZnGO, suggesting a more complex porous structure.



Fig. 5.40 Nitrogen adsorption isotherm

The pore size distribution (Fig. 5.41), obtained using BJH method, shows the heterogeneity of pore sizes, with no volume of micropores (<2 nm) and a wide distribution of large mesopores, with a predominant size of about 15–35 nm. The addition of AuNPs resulted in a slight decrease in the pore sizes and in the formation of small volume of pores with sizes less than 10 nm. On the contrary, the addition of AgNPs led to an increment in the pore sizes, with a decrease in the volume of the mesopores.

The parameters of the porous structure calculated from the isotherms are summarized in Fig. 5.42. The surface area of AuZnGO increased by 13.4% and the total pore volume of about 4%, compared to those parameters for ZnGO. For AgZnGO, both surface area and total pore volume decreased by 10 and 7%, respectively, compared to ZnGO. That results suggest that the addition of AuNPs leads to a higher dispersion of the inorganic phase around the GO. The formation of



Fig. 5.41 Pore size distribution calculated using the BJH model



Fig. 5.42 Parameters of porous structure calculated from the nitrogen adsorption isotherms

nanosized zinc (hydr)oxide particles can be another reason why AuZnGO exhibited the highest values of surface area and porosity.

5.1.4.3 Surface Chemistry Analysis

The amount of the terminal and bridging oxygen-containing groups calculated from the results of potentiometric titration is collected in Fig. 5.43. Compared to ZnGO,



Fig. 5.43 Amounts of terminal and bridging oxygen-containing groups detected by potentiometric titration experiments

the addition of NPs resulted in an increase in the number of the bridging oxygen groups by 96 and 81% for AuZnGO and AgZnGO, respectively. This increase can be linked to the formation of zinc oxide phase, due to the altered nucleation. The addition of AuNPs did not alter the amount of terminal hydroxyl groups. On the contrary, the addition of AgNPs resulted in a decrease of terminal groups by 22% as compared to ZnGO. The ratios of the terminal to bridging OH groups are 5.1, 2.7, and 2.3 for ZnGO, AuZnGO, and AgZnGO, respectively. This supports the finding that the addition of the nanoparticles led to an increase in the ZnO phase. The total amount of the oxygen-containing groups detected using potentiometric titration was the highest for AuZnGO, as a result of the enhanced dispersion of the zinc (hydr) oxide phase and the nanoscaled particles.

The element maps for the composites (Fig. 5.44) further support the high dispersion of NPs on the surface. For both composites, the absence of chloride (<0.2%) indicates that the NPs did not react with chloride from the initial ZnCl₂ solution. The comparison of the Au and Ag amounts on the surface showed than in the case of AgZnGO, the AgNPs are mostly dispersed on the outer surface of the composites.

5.1.4.4 Estimation of Reactive Oxygen Species

In order to acquire additional perceptions into the reactive oxygen species (ROS) that can be involved into the detoxification/decomposition reactions on our catalysts, the ability of the samples to generate hydroxyl radicals (⁻OH) and superoxide radicals was evaluated at ambient light and in dark. Terephthalate



Fig. 5.44 EDX elemental mapping of AuZnGO and AgZnGO



Fig. 5.45 Analysis of the changes in the intensity of the emission at 425 nm (formation kinetics of THA) with an increase in the experimental time under ambient light irradiation

(TA) can be converted to HTA at the presence of hydroxyl radicals, and the latter has a characteristic emission at 425 nm [65]. The ability to promote the formation of \neg OH was evaluated by analyzing the fluorescence intensity of hydroxyl terephthalate (HTA) after various intervals of time (10, 30, 60, 120, 180, and 240 min) for all samples. The changes in the fluorescence spectra of the TA solution mixed with AuZnGO and AgZnGO are shown in Fig. 5.45. It can be clearly concluded that the fluorescence intensity at 425 nm increased only for AgZnGO. ZnGO and AuZnGO show the same behavior. No sample was able to form hydroxyl radical in dark.

The ability of the samples to form superoxide species had been investigated by monitoring the nitro blue tetrazolium (NBT) degradation by UV–Vis spectroscopy. No material was found to promote the degradation of NBT either under light or in dark conditions, since the emission of the solution remained unchanged even after 4 h.

5.1.4.5 Study of the Kinetics and the Maximum Detoxification Performance

The main goal of the addition of the NPs was to enhance further the photocatalytic performance of the ZnGO composite, which showed a supreme detoxification performance, especially after 8 days of exposure. For that reason, the detoxification tests were held under ambient light irradiation. In order to achieve the maximum evaporation of the injected liquid CEES, to examine the kinetics of the weight uptakes, and



Fig. 5.46 Mass uptakes/adsorption capacities measured at visible light for up to ten days

to monitor the evolution of the formed products, the adsorption tests were carried out for up to ten days. The weight uptakes were recorded and are collected in Fig. 5.46.

The mass uptakes increase almost linearly for all samples until the eighth day. Interestingly, the maximum weight uptake was found after 9 days for AgZnGO that has the smallest surface area, total pore volume, and amount of terminal hydroxyl groups. AuZnGO also showed higher maximum weight uptake than did ZnGO. These facts elucidate that the addition of the nanoparticles into the composites plays a beneficial role on the degradation ability, which apparently does not depend on the porosity and the number of surface functional groups.

5.1.4.6 Monitoring the Evolution of the Volatile Products in the Headspace

Since the weight uptakes suggested that the reactions that occur during the adsorption plays a crucial role in governing the adsorption capability, the formation of the volatile products was monitored and their amounts were compared semiquantitatively. The chromatograms of AgZnGO and AuZnGO are shown in Fig. 5.47. Comparison of the intensities of the peaks related to CEES (at retention time slightly higher than 5 min) suggests that AgZnGO interacts faster with the vapors of the surrogate than does AuZnGO since for all the time intervals the intensity of this peak was lower than the one for the latter sample. After 9 days, no CEES was detected in the headspace of AgZnGO. On the contrary, for AuZnGO, the peaks related to CEES showed higher intensities after the same exposure time. The main two detected peaks at the retention time of about 2 min are from ethyl vinyl sulfide (EVS) and divinyl sulfide (DVS). In the case of AuZnGO, these peaks totally disappeared after 9 days of interactions, suggesting that even the formed products degraded further or retained on the surface.



Fig. 5.47 Mass uptakes/adsorption capacities measured at visible light for up to ten days of CEES exposure

A further comprehensive analysis of the chromatograms suggested that more compounds can be identified based on the chromatograms (Fig. 5.48). All the identified species in the headspace along with their characteristic mass-to-charge ratios (m/z), names, chemical formulas, abbreviations, and boiling points are collected in Table 5.4. It is important to mention that all seven volatile compounds detected are non-toxic or significantly less toxic when compared to CEES.



Fig. 5.48 Analysis of the chromatograms at specific retention time ranges

Name	Linear formula	Abbrev.	b. p. (°C)	Characteristic mass-to-charge ratio (m/z)
2-chloroethyl ethyl sulfide	CH ₃ CH ₂ SCH ₂ CH ₂ Cl	CEES	156	124, 109, 89, 75, 61, 47
Ethyl vinyl sulfide	CH ₃ CH ₂ SCH=CH ₂	EVS	98	88, 73, 60, 59, 45
Divinyl sulfide	CH ₂ =CHSCH=CH ₂	DVS	84	86, 85, 71, 59, 41, 40
Diethyl disulfide	CH ₃ CH ₂ SSCH ₂ CH ₃	DEDS	110	122, 94, 66, 60, 47, 45
1,2-bis (ethylthio) ethane	CH ₃ CH ₂ SCH ₂ CH ₂ SCH ₂ CH ₃	BETE	218	150, 122, 90, 75, 61, 47
Methyl vinyl sulfide	CH ₂ =CHSCH ₃	MVS	69	74, 59, 47, 44, 40
Acetaldehyde	CH ₃ CHO	MeCHO	20	44, 43, 42
Ethanol	CH ₃ CH ₂ OH	EtOH	78	46, 45, 43, 42

Table 5.4 Details on the detected compounds in the headspace

The detected products are arbitrarily classified into three categories (Fig. 5.49) based on their molecular weight (Mw). The first group includes the vinylic compounds EVS and DVS, which have similar Mw. They are formed in the dehydrohalogenation reactions. The second group contains the species with smaller Mw than CEES (MVS, EtOH, and MeCHO). For the formation of these species, cleavage of C–C or S–C bond has to take place.



Fig. 5.49 Arbitrarily classification of the detected volatile compounds in the headspace

Oxidation was also acquired for the formation of ethanol and acetaldehyde. The third group includes molecules with notably higher Mw than that of CEES (DEDS and BETE). For the formation of these compounds, S–C cleavage is expected to take place and to be followed by a dimerization.

The trends in the concentration of the six detected compounds in the headspace (peak areas) with the progress of adsorption are shown in Fig. 5.50. The results indicate that various interactions/reactions between CEES and the surface of the samples were taking place simultaneously, although EVS is the predominant degradation product. The composites with the nanoparticles showed significantly higher reactivity as can be observed from the peak areas of EVS and DVS. In the case of single ZnGO composites, MVS was also detected in a limited quantity. This compound was not detected for AuZnGO and AgZnGO, suggesting that it gets degraded fast. The comparison of the peak areas between the two multicomposites showed that AgZnGO showed higher formation rate for the vinylic products, EVS, and DVS.

The areas of the peaks representing products from the dimerization showed similar trends. Interestingly, only on AuNPs the formation of MeCHO and EtOH is promoted, as a result of photooxidation, since the latter compounds was not detected when the tests were performed in dark. The enhanced photocatalytic performance by NPs addition was reported also for other metal oxides, since NPs can introduce a surface plasmon resonance effect [66–68].



Fig. 5.50 Dependence of the area of the chromatographic peak (analysis of the headspace) for the particular compounds on the exposure time under light irradiation

5.1.4.7 Detoxification and Adsorption Mechanisms

The proposed reaction pathways that take place during the CEES reactive adsorption process are collected in Fig. 5.51. The formation of the predominant vinylic product, EVS, can occur through two pathways. In the first one (pathway 1), the Zn(II) centers act as Lewis acids and promote the cleavage of the C-Cl bond [2, 69]. The formed diethyl sulfonium cation (DES⁺) gets converted to an unstable intermediate cyclic cation, through an intermolecular cyclization process. Afterward, the cyclic alkyl sulfide cation is rearranged via a bimolecular elimination (E2) pathway, which leads to the formation of EVS, with the simultaneous elimination of a labile hydrogen atom by a hydroxyl group. The formation of water was also aforementioned in the previous sub-chapter, as well as in the case of the adsorption of CEES on $Fe(OH)_3$ [1, 69], and can explain the gel-like form of the exhausted samples after 7 days of exposure. The second pathway (pathway 2) involves the formation of a diethyl sulfide radical, which undergoes a further intermolecular electrons rearrangement to form EVS. This pathway can be the reason of the higher amount of EVS detected in the headspace for the NPs containing composites than that of ZnGO, as a result of higher photoreactivity by the addition of the NPs.

The formation of DEDS, BETE, ethanol, and acetaldehyde can be attributed to the third pathway included in Fig. 4.16 (pathway 3). The α -carbon radical thioether can be protonated to α -carbon radical thioether cation. The reaction of the latter with an activated hydroxyl groups can lead to ethyl sulfide radical and ethanol. The sulfide radical can react with another sulfide radical or a diethyl sulfide radical,



Fig. 5.51 Proposed reactions that take place during the CEES reactive adsorption process

resulting in the formation of the products with two sulfide atoms and higher Mw than CEES (DEDS and BETE). The limited detected amount of ethanol in the headspace for AgZnGO can be due to its strong retention on the surface by hydrogen bonds without additional oxidation to aldehyde. Further photooxidation of the EtOH to acetaldehyde was found only on AuZnGO. AuNPs in the structure of the multicomposite altered the chemical environment and activated the oxygen-containing groups of the inorganic phase, which can photooxidize ethanol. It is of paramount importance to mention that no other oxidation products, such as sulfoxide or sulfone, were detected.

DVS can be formed in two pathways (pathways 4 and 5). In the first one, CEES is transformed to a radical by a photoexcited electron or a formed hole, and through an intermolecular electron rearrangement, it gets further transformed to chloroethyl vinyl sulfide. The latter is converted to DVS, following the same pathway as described for the first formation pathway of EVS. The hydroxyl radicals can convert EVS to DVS via an intermediate diethyl sulfide radical (pathway 5). The high amount of DVS in the headspace of AgZnGO can be linked to this pathway, since only this composite revealed the ability to form hydroxyl radicals. Finally, these radicals can react with diethyl sulfide radicals, forming hydroxyl ethyl ethyl sulfide (HEES). Indeed, the analysis of the extracts showed a significantly higher amount of HEES for AgZnGO compared to other two samples.

5.1.4.8 Conclusions

The simultaneous incorporation of AgNPs or AuNPs during the synthesis of zinc hydroxide/GO composite resulted in the formation of composites with improved adsorption/detoxification performance against the surrogate of mustard gas, CEES, under visible light irradiation. The nanoparticles altered also the nucleation pathway. The composite consisted of AgNPs revealed two distinguished crystallographic phases, orthorhombic zinc hydroxide, and zinc oxide nanorods that created a cobweb-like network. In the case of AuNPs addition, the resulted amorphous crystallographic phase consisted of zinc (hydr)oxide nanoparticles, which surrounded the GO phase. The detectable on the outer surface NPs maintained their spherical shape. It is plausible to assume that the existence of NPs on the outer phase promoted the photoreactivity, altered the chemical environment, and activated the oxygen species. Addition of NPs caused increases in the following:

- (1) chemical and structural surface heterogeneity;
- (2) amount of highly reactive terminal groups;
- (3) activity of the oxygen-containing surface groups;
- (4) separation of electron/holes pair, preventing their recombination;
- (5) photocatalytic detoxification performance.

The addition of AgNPs resulted in the highest weight uptake and photodegradation yield, even though this composite showed the lowest porosity. AgNPs incorporation promoted also the ability of the hydroxyl radicals' formation. On the other hand, the addition of AuNPs showed lower weight uptake performance compared to AgNPs addition, but introduced a selective photooxidation ability. Only ethanol oxidized to acetaldehyde, and no sulfoxides or highly toxic sulfones were formed. This can be explained by the introduction of a surface plasmon effect. Since AuNPs and AgNPs have a relatively high cost, other non-noble metal NPs probably would be able to replace their function in the composites.

5.2 Zirconium (Hydr)Oxide-Based Multifunctional Nanocomposites



Section 5.2.1 is adapted from Ref. [70] with permission from the Royal Society of Chemistry.

5.2.1 Effect of GO Phase in ZR(OH)₄/GO Composites on the Extent of Catalytic Reactive Adsorption

5.2.1.1 Materials and Objectives

The main goal of this study was to prepare zirconium (hydr)oxide and its composites with various amounts of graphite oxide (GO), using a controlled rate precipitation method, and to evaluate their ability for the removal of CEES vapors at ambient conditions. Additional objectives were to identify the optimal amount of the carbonaceous phase, which could lead to the greatest enhancement in the performance as adsorbents and catalysts, and to determine how the structural and chemical properties which affect the detoxification ability and the reactive adsorption mechanism.

5.2.1.2 Structural and Morphological Characterizations

X-ray diffraction patterns of all samples are shown in Fig. 5.52. Regardless of the presence and amount of GO, all samples are amorphous. Moreover, the characteristic diffraction peak of graphite oxide at 11.6° 2 Θ is not seen, indicating an exfoliation of GO within the amorphous structure of zirconium hydroxide.

The structural parameters calculated from measured nitrogen adsorption isotherms are shown in Fig. 5.53. If the final products were a physical mixture, an increase in the GO content would lead to a decreased porosity of the synthesized materials, since the surface area of GO is only 4 m²/g and its total pore volume is 0.002 cm^3 /g [71]. The hypothetical surface areas and total pore volumes were calculated assuming a physical mixture of both components and their percentage contribution to the values analyzed. The comparison of the parameters of the porous structure is shown in Fig. 5.53b, c. The synergistic effect of the composite formation on the porosity development is clearly seen from the comparison of the measured and hypothetical values. The most visible differences are those for ZrGO5 (+ 36%) and ZrGO20 (+42%). The measured surface area of the former is 29% higher than that of ZrOH. The increases for ZrGO1, ZrGO10, and ZrGO20 were 4, 18, and 16%, respectively.

The addition of GO led also to a significant alteration in the total pore volumes, especially in the volume of mesopores. It is worth mentioning that all materials are



Fig. 5.52 X-ray diffraction patterns for the initial samples. (Reproduced from Ref. [70] with permission from the Royal Society of Chemistry)



Fig. 5.53 a Nitrogen adsorption isotherms; **b** comparison of the measured and hypothetical surface areas; **c** micro- and mesopores volumes, and **d** pore size distributions. (Adapted from Ref. [70] with permission from the Royal Society of Chemistry)

both a micro- and mesoporous as shown in Fig. 5.53d. The ratio of the micropore to mesopore volumes decreased with the addition of GO (Fig. 5.53c). While the addition of 1% GO to ZrOH affected only slightly the volume of the pores, the increase in the pore volume of ZrGO5 was the most pronounced. Its pore volumes are 17, 83, and 52% higher than V_{mic} , V_{mes} , and V_{Total} for ZrOH, respectively. For the composites with 10 and 20% of GO, the increase in the pore volume is less pronounced than that for ZrGO5. The results indicate that 5% GO is the critical/ optimal amount for the development of the high porosity.

The SEM images (Fig. 5.54) show the heterogeneous features of the zirconium (hydro)oxide surface. Smaller zirconium hydroxide particles than those in ZrOH were observed after the addition of 1% GO. The GO flakes were surrounded by the inorganic phase. Further increase in the GO content enhances the dispersion of the inorganic phase around GO and encapsulates more GO in the formed particles.



Fig. 5.54 SEM images of the samples' morphology. (Reproduced from Ref. [70] with permission from the Royal Society of Chemistry)

5.2.1.3 Surface Chemistry Analysis

The amount of surface functional groups was estimated by the potentiometric titration method. In the case of ZrOH, they can be grouped into two categories: those with pK_a between 7 and 9, and those with pK_a higher than 9. The first ones

are linked to oxygen bridging groups and coordinated water, and the second ones to hydroxyl terminal groups [72, 73]. It was reported that the terminal hydroxyl groups played a key role in the adsorption of CEES vapors on zinc and iron (hydr) oxide [1, 13]. They were also found crucial for the removal of VX nerve agent on $Zr(OH)_4$ [25] and of H₂S on metal (hydr)oxides [16, 74, 75]. The results of potentiometric titration (Fig. 5.55) clearly revealed that the addition of GO increased the total number of functional groups, especially of the terminal hydroxyl groups. The most pronounced increase was found for ZrGO5, which has the highest number of surface acidic species. Compared to ZrOH, the number of terminal hydroxyl groups increased by 141% and the number of bridging groups by 56%. Interestingly, the composite with 1% GO showed almost the same number of groups as did ZrGO5. A further addition of the carbonaceous phase led to a decrease in the number of surface groups; however, the amount of total groups was always higher than that on ZrOH. It is worth to mention that the synergistic effect of the composite formation on the amount of functional groups on the surface is also seen from the comparison of their measured and hypothetical values calculated assuming the physical mixture. Since the total number of functional groups of GO in the pK_a range 7–11 is 2.009 mmol/g, the measured amounts of functional groups are higher than the hypothetical values by 95, 91, 36, and 1% for ZrGO1, ZrGO5, ZrGO10, and ZrGO20, respectively.

The above-mentioned results indicate that 5% GO is the optimum amount resulting in the composite with both highest porosity and richest surface chemistry. Thus, the addition of GO plays an important role in increasing the dispersion and amorphicity of the inorganic phase.



Fig. 5.55 Amounts of bridging and terminal groups measured by potentiometric titration. (Reproduced from Ref. [70] with permission from the Royal Society of Chemistry)

The differential thermal gravimetric (DTG) curves for ZrOH and the composites are collected in Fig. 5.56a. All the samples showed a gradual weight loss from a low temperature up to 400 °C. The weight loss until 125 °C can be linked to the removal of the water, coordinated as ligands or physically adsorbed. The dehydroxylation of the complex hydroxide structure of zirconium hydroxide to the bridged structure occurs above 125 °C. (Fig. 5.56b). The decomposition of the epoxy groups of GO is visible between 190 and 210 °C for the samples with more than 10% of GO, while this decomposition is barely detected for ZrGO5 [16, 54, 73]. The sharp peaks



Fig. 5.56 DTG curves measured in helium for the initial samples (**a**), and a stereo-view of the dehydration of the hydrated zirconium hydroxide (**b**). (Reproduced from Ref. [70] with permission from the Royal Society of Chemistry)

between 450 and 650 °C, with a limited intensity, can be assigned to the formation of metastable tetragonal or monoclinic zirconium oxide [72, 76].

Clearfield et al. first showed that the addition of a base to ZrOCl₂*8H₂O leads to the formation of a polymeric oxohydroxide with the general formula $[ZrO_{b}(OH)_{4,2b}$. xH₂O] [77, 78]. This structure (Fig. 5.56b) contains four types of oxygen groups. On the outer phase of the structure, the terminal -OH groups and coordinated water molecules are located on the outer phase of the structure. In the interior part of the matrix, the Zr atoms are connected via bridging OH or oxygen groups. The existence of both types of OH groups was also reported by Huang et al. for $Zr(OH)_4$ and by Chitrakar et al. in the case of ZrO(OH)₂•(NaO)_{0.005}•1.5H₂O [76, 78]. Zirconium hydroxide reported in the literature revealed a broad weight loss up to 400 $^{\circ}$ C, which was linked to the dehydration. Assuming the existence of pure Zr(OH)₄, its thermal transformation to ZrO₂ should lead to a 22.6% weight loss. In our case, the weight loss of unmodified ZrOH was 16.7% up to 450 °C. This indicates that our materials have the random amorphous structure of hydrate zirconium (hydr)oxide instead of zirconium oxide. The terminal -OH groups are proved to be more active for adsorption/ degradation of the organic molecules. Owing to their position in the lattice, they may interact faster with CEES, while the bridging groups are less active and will interact slower, since the diffusion into the lattice requires a longer time [78].

5.2.1.4 Adsorption Performance and the Optimum Amount of GO

All studied samples were evaluated as adsorbents of 2-chloroethyl ethyl sulfide vapors. The measured weight gains are collected in Fig. 5.57. Owing to the negligible adsorption capacity of GO (7 mg/g), the hypothetical weight gains, assuming the formation of a physical mixture instead of a composite, for the adsorption capacity were expected to decrease with the increasing GO content. On



Fig. 5.57 Weight gains for the tested materials

the contrary, all composites revealed greater weight gains than that for ZrOH, showing a significant synergetic effect of the composite formation. The largest weight gain was found for ZrGO5, and it is 67% higher than that of ZrOH and 75% higher than that calculated for the hypothetical physical mixture of the composite components. The amounts adsorbed on ZrGO1, ZrGO10, and ZrGO20 were higher than that on ZrOH by 9, 39, and 28%, respectively. The adsorption tests were held also in dark and the measured weight uptakes showed the same values with those measured under light irradiation.

5.2.1.5 Role of the Textural Parameters and Surface Chemistry

The dependences of the weight gain upon exposure to CEES for 24 h on the surface area, on the number of terminal hydroxyl groups, and on mesopore volume are shown in Fig. 5.58. Linear correlations suggest that these factors play important roles in the reactive adsorption process. No correlation of the capacity on micropore volume and bridging groups was found.

5.2.1.6 Characterizations of the Exhausted Samples

The changes in surface chemistry after the exposure to CEES were evaluated from the FTIR spectra (Fig. 5.59). The characteristic vibrations for zirconium hydroxide



Fig. 5.58 Dependence of the weight gain on the surface area (a), terminal groups (b) and the mesopore volume (c) for 24 h of CEES exposure. (Reproduced from Ref. [70] with permission from the Royal Society of Chemistry)

appear at 1590, 1390, and 854 cm⁻¹. The broad band with a maximum at 1590 cm^{-1} can be assigned to the hydroxyl groups of water molecules and at 1390 cm⁻¹ to O-H vibration from Zr–OH [72, 73]. The small band at 854 cm⁻¹ is attributed to the lattice vibration of a Zr–O bond. For graphite oxide, the stretching vibration of C-O bonds from carboxylic groups, bending vibration of O-H from hydroxyl/phenol groups, and O-H vibration of water appear at 1050, 1390, and 1630 cm^{-1} , respectively. The band at 990 cm⁻¹ corresponds to epoxy/peroxide groups, while the band at 1730 cm^{-1} is characteristic of a C=O stretching vibration in carboxylic acids. The band at 1228 cm^{-1} might be related to C–O vibrations in epoxides. The vibrations of oxygen groups from graphite oxide are not visible for the composites with the low GO content (1, 5 and 10%) owing to the involvement of these groups in the formation of the composites. For the sample with 20% GO, only one broad peak at 1000 cm⁻¹ appeared that corresponds to the vibration of epoxy/peroxide groups. The characteristic bands of zirconium hydroxide are visible for all samples. The exhausted samples are referred to with letter E added to their names. After the CEES vapor adsorption, the intensities of the bands at 850, 1390, and 1590 decrease, indicating that the -OH groups and the water molecules participate in the reactive adsorption.

The differential thermal gravimetric (DTG) curves for the exhausted samples are shown in Fig. 5.60. The formation of new compounds after the reactive adsorption is evident since four new peaks which appear at 110, 170, 270, and 300 °C with



Fig. 5.59 FTIR spectra of the initial and exhausted (-E) samples. (Reproduced from Ref. [70] with permission from the Royal Society of Chemistry)



Fig. 5.60 DTG curves in helium for the exhausted samples. (Reproduced from Ref. [70] with permission from the Royal Society of Chemistry)

various intensities for all exhausted samples. We refer to them as peaks 1, 2, 3, and 4, respectively. Mass spectrometry of the exhaust gases/vapors was carried out simultaneously with the TA analysis in order to determine the origin of these new peaks. The assignment discussed below is based on the detected m/z fragments. The MS thermal profiles for ZrOH are collected in Fig. 5.61. Nomenclature, abbreviations, and details on the detected compounds are collected in Table 5.5.

Based on the m/z thermal profiles, the Peak 1 at the DTG curve with a maximum at 110 °C is assigned to CEES (m/z: 90, 75, 61, 47) and to the compounds with identical series of main-intense m/z signals. The latter species include BETE, HEES, and/or saturated sulfides such as EES. Moreover, it can be also assigned to EVS (m/z: 88, 73, 59, 45) and DEDS (m/z: 66, 60, 47). Peak 2 with a maximum at 170 °C is related to the dehydroxylation, since only the profile of OH (m/z: 17) gives signal at this temperature. The lower intensity of this peak and the higher temperature of the decomposition, compared to those for the initial sample, suggest that the hydroxide groups are involved in the adsorption/degradation of CWA and they are stabilized by interactions, such as polar or hydrogen bonds, with the organic molecules. Moreover, for the composition of GO in the same temperature range contributes to an increase in the





Name	Chemical formula	Abbreviation	Characteristic mass-to-charge ratio (m/z)
2-chloroethyl ethyl sulfide	CH ₃ CH ₂ SCH ₂ CH ₂ Cl	CEES	124, 109, 90, 75, 61, 47
2-hydroxyethyl ethyl sulfide	CH ₃ CH ₂ SCH ₂ CH ₂ OH	HEES	106, 90, 75, 61, 47
1,2-bis (ethylthio) ethane	CH ₃ CH ₂ SCH ₂ CH ₂ SCH ₂ CH ₃	BETE	150, 122, 90, 75, 61, 47
Ethyl ethyl sulfide	CH ₃ CH ₂ SCH ₂ CH ₃	EES	90, 75, 61, 47
Ethyl vinyl sulfide	CH ₃ CH ₂ SCH=CH ₂	EVS	88, 73, 59, 45
Diethyl disulfide	CH ₃ CH ₂ SSCH ₂ CH ₃	DEDS	122, 94, 66, 60, 47, 45
1,4-butanedithiol	SHCH ₂ CH ₂ CH ₂ CH ₂ SH	BDT	122, 88, 73, 60, 55, 47

Table 5.5 Details on the detected compounds on the surface and in the headspace

intensity of Peak 2. Peak 3 (maximum at 270 °C) likely represents DEDS and BDT, since m/z 55 which is characteristic for the later compounds appears only at this temperature. Peak 4 at 300 °C can be linked to CEES, HEES, BETE, EES, and EVS. The existence of two decomposition temperatures for the same compound is linked to the adsorption at two energetically different sites [79]. The first one, at a lower temperature, represents weakly adsorbed molecules, likely via polar forces on the external surface and/or in the mesopores, and the second one—the removal of strongly adsorbed molecules in the micropores or those hydrogen bonded to the –OH groups. The same trends for the removal of CEES and EVS were found for the adsorption of CEES on iron and zinc (hydr)oxides [1, 69].

For ZrOH, the evolution of the m/z signals corresponding to Cl (m/z: 35) supports the removal of CEES at two different temperatures seen by two maxima at 100 and 300 °C. Moreover, a small maximum at temperature lower than 60 °C is linked to the formation of small molecules containing chloride and a stable signal above 600 °C can be assigned to the decomposition of the Zr–Cl bonds. Finally, the evolution of the m/z signals of SO₂ (m/z: 64), CH₃ (m/z:15), and carbon (m/z: 12) further supports the decomposition of a variety of compounds at the aforementioned temperatures. The acquired m/z thermal profiles for the composites show the same origin of the new peaks. Since many compounds can be formed upon heating during the TA analysis, this method does not provide enough evidence for the mechanism and the progress of the reactive adsorption process.

5.2.1.7 Evaluation of the Detoxification Performance

In order to determine the maximum weight uptake and to analyze the progress of reactive adsorption, different CEES exposure times were studied (Fig. 5.62). Since
ZrGO5 showed the best performance for CEES adsorption after 24 and 48 h among all others composites tested, this sample along with ZrOH was chosen to study the extent of the adsorption in more detail. ZrOH reached the maximum weight uptake after 36 h (105 \pm 6.2 mg/g). For ZrGO5, the maximum weight uptake was revealed after 48 h with almost twice more weight increase (204 \pm 8.3 mg/g) than that of ZrOH. For the other composites, the weight increases after 24 and 48 h of CEES exposure are also included in Fig. 5.62. The results show that the graphene phase enhanced the amount of CEES adsorbed and/or the amount of the degradation products adsorbed on the surface.

The correlations of the maximum uptakes (at 48 h) with the surface area, mesopore volume, and number of the terminal groups showed linear trends, with R^2 values 0.97, 0.98, and 0.96, respectively (Fig. 5.63). The results indicate that both the chemical and physical features of the materials play a key role in the adsorption performance, suggesting that both chemical and physical interactions are involved in the reactive adsorption process. The increased porosity and the amount of the surface groups of ZrGO5 lead to a fast weight gain. It has to be mentioned here that long adsorption times are only apparent, since a low vapor pressure of CEES causes that a considerable length of time is required for its evaporation. Prasad et al. reported that in order to reach the maximum weight uptake of mustard gas on an activated carbon (with surface area 1250 m²/g), 576 h (24 days) were needed [80].

5.2.1.8 Identification of the Volatile Products in the Headspace

An increase in the exposure time to 48 h increased the amount of CEES and/or of its decomposition products adsorbed. It is likely due to slow transformations, which





Fig. 5.63 Dependence of the maximum weight gain on the surface area (a), terminal groups (b), and the mesopore volume (c) after 48 h of CEES exposure. (Reproduced from Ref. [70] with permission from the Royal Society of Chemistry)

take place on the surface of the materials, or due to the time needed for the evaporation of CEES. Even though the adsorption performance can be evaluated by the measured weight increase, the latter cannot provide sufficient sole evidence about the activities and the mechanism of the interactions. Therefore, to study in detail the interactions and to throw light on the products of surface reactions, the headspace of the closed adsorption system and the extracts from the surface of the exhausted materials were analyzed by GC-MS. As mentioned above, the analysis focused on of ZrGO5 and ZrOH. For both ZrOH and ZrGO5, CEES in the headspace was detected at the elusion time of 3.3 min, EVS at 1.8 min, and BETE at 4.8 min. The chromatograms after 48 h are shown in Fig. 5.64 A. The intense peak at 3.3 min indicates that the marked amount of CEES vapors is still present in the reaction vessel even after 48 h. The low intensities of the peaks representing EVS and BETE are due to the saturation of the headspace with CEES or due to their adsorption on the surface of the materials.

The trends in the concentration of EVS and BETE in the headspace (represented by peak areas) with the progress of adsorption are shown in Fig. 5.64 B and C. The results suggest that various interactions/reactions between CEES and the surface of the samples take place simultaneously. The continuous increase in the amount of EVS detected in the headspace is in agreement the TA-MS results. This indicates that the degradation of CEES leads mainly to the dehydrohalogenation products (Fig. 5.65). Briefly, CEES can be transformed to a transient cyclic sulfonium cation



Fig. 5.64 Chromatograms of the headspace for ZrOH and ZrGO5 after 48 h of CEES exposure (a) and dependence of the area of the chromatographic peak (analysis of the headspace) of EVS (b) and BETE (c) on the exposure time. (Reproduced from Ref. [70] with permission from the Royal Society of Chemistry)

by an intermolecular cyclization process. Sulfur atom acts as a nucleophile and attacks the electrophilic carbon to which the chloride is bonded. Afterward, via a bimolecular elimination (E2) reaction, a labile hydrogen from the cyclic cation transfers to a negatively charged lattice oxygen of the zirconium phase, which acts as a Lewis base. The cleavage of the C–Cl bond in the first step of this elimination pathway is promoted by the Lewis acidic Zr(IV) centers. The analogous degradation pathway was reported for the adsorption of CEES or HD on aluminum oxide, zinc hydroxide, and iron oxyhydroxide [1, 47, 69]. The thermal profile of m/z 35



Fig. 5.65 Dehydrohalogenation of CEES to EVS by an intermediate cyclic sulfonium cation. (Reproduced from Ref. [70] with permission from the Royal Society of Chemistry)

shows a strong signal at the temperature of $ZrCl_4$ decomposition (330 °C) owing to the bonds between the chlorine atoms and the inorganic matrix as a result of the intermolecular cyclization process.

The trend in the BETE concentration was opposite compared to that for EVS. A decrease of its concentration in the headspace can be linked to both its limited formation and simultaneous strong retention on the surface. The mechanism of the BETE formation includes the cleavage of S–C bond and the formation of a new S–C bond between two distinct molecules. Alkoxy species on the surface react with sulfonium cations, resulting in the formation of BETE and $-OCH_2CH_3$ groups. The involvement of the oxygen-containing groups in the formation of the alkoxy species is supported by the FTIR spectra, in which a decrease in the intensity of the bands assigned to the -OH was found. Verma et al. reported the formation of EVS and alkoxy species after the interaction of CEES with the isolated hydroxyl groups on ZrO_2 or WO₃ nanoparticles [81, 82].

The aforementioned pathways require the adsorption of CEES on the surface as a first step. As it was suggested from the TA analysis, there are two diverse adsorption centers with different energies for both CEES adsorption and EVS adsorption. The lower energetically adsorption process likely includes the polar interaction of $S^{\delta-}$ with the $Zr^{\delta+}$ [45, 69]. Stronger adsorption can be due to the formation of hydrogen bonds between the OH groups of the materials and both S and Cl moieties of the organic molecules. Panayotov and Yates studied in detail the adsorption of CEES on a high surface area TiO₂-SiO₂ mixed oxide, and they found that hydrogen bonding of this molecule to Si–OH groups occurs through both Cl and S moieties [38]. The removal of the adsorbed molecules at low temperature (110 °C) in the TA-MS analysis is linked to the weak interactions and at higher temperature (300 °C)—to the hydrogen-bonding interactions.

5.2.1.9 Identification of the Surface Reaction Products Retained on the Surface

The analysis of the surface extracts by GC-MS revealed the existence of both CEES and BETE. It is worth to mention that the signal related to BETE has higher intensity in the chromatograms of the extracts than those of the headspace. The areas corresponding to BETE consist of 16–20% of the total areas of all detected compounds, while these values were in the range of 1–3% from the analysis of the headspace. HEES, disulfides such as DEDS and BDT, or any oxidation products such as sulfoxides and sulfones were not detected either in the headspace or in the extracts. The possible detection some of them (such as BDT, DEDS) from the TA-MS analysis can be due to the thermal transformation during the analysis and the involvement of the released oxygen in their formation. Finally, the higher concentrations of BETE in the extracts of the composites, than in that of ZrOH, further support our finding that the addition of GO leads to a significant increase in the extent of reactive adsorption and in the selective catalytic transformation of CEES to EVS and BETE. It is due to the alterations of the active surface sites and

chemical heterogeneity of the composites. The increased dispersion of the hydroxyl groups and the developed porosity play the key roles in the detoxification process.

5.2.1.10 Detoxification Mechanism

All the above-mentioned interactions of CEES and of its degradation by-products with the samples' surfaces are shown in Fig. 5.66. The amorphous zirconium hydroxide phase acts as a reactive adsorbent, since it physically adsorbs the organic molecules and catalytically transforms CEES to the dehydrohalogenation product, EVS, and to the polymerization product, BETE.

5.2.1.11 Conclusions

The results presented in this chapter showed for the first time that zirconium (hydr) oxide and its composites with graphite oxide can be used as reactive adsorbents of the mustard gas surrogate vapors. The aqueous synthetic route leads to the materials with amorphous nature, various levels of complexity, a relatively high surface area,



Fig. 5.66 Proposed reactions scheme of CEES reactive adsorption mechanism. (Reproduced from Ref. [70] with permission from the Royal Society of Chemistry)

and a high density of active hydroxyl group. The addition of GO resulted in an increased degree of the structural and chemical heterogeneity. The most pronounced increases in the surface area (+141%) and in the number of terminal hydroxyl groups (+67%) compared to the pure zirconium hydroxide were found for the composite with 5% GO (ZrGO5).

Notably, the unmodified zirconium (hydr)oxide showed the highest weight uptake in comparison with those reported in the literature for hydrous ferric oxide and zinc hydroxide (at the same conditions for 24 h). ZrGO5 showed the best adsorption performance (155 mg/g after 24 h and 205 mg/g after 48 h). The results indicate the paramount role of surface chemistry and porosity in the reactive adsorption process of CEES.

Based on the collected results, two steps removal of CEES were proposed. The first one involves the retention of the organic molecules by physical forces, and the second includes the catalytic and selective transformation of CEES to ethyl vinyl sulfide by dehydrohalogenation and to 1,2-bis(ethylthio) ethane by degradation/ dimerization. The conversion rates on the composites with carbonaceous phase were also higher than that on the unmodified sample.

5.2.2 AgNPs Embedded in Zirconium Hydroxide/GO Composites

5.2.2.1 Materials and Objectives

The objective of this particular study was to investigate whether or not the addition of AgNPs further enhances the catalytic detoxification performance, as a result of a plasmon effect or of the structural and chemical features alteration. For that reason, the composites of zirconium hydroxide with AgNPs and with or without GO were synthesized. 5% of GO was chosen, since this amount of carbonaceous phase showed the best performance, while the amount of AgNPs was 1 wt% of the final mass. The composites of $Zr(OH)_4$ and AgNPs are referred to as AgZrOH and AgZrGO, with the absence or presence of GO, respectively. For the sake of comparison, the results for pure zirconium hydroxide (ZrOH) and the composite with 5% GO (ZrGO) addressed above are included to the discussion.

5.2.2.2 Structural and Morphological Characterization

The XRD powder diffraction patterns are collected in Fig. 5.67. All samples show a high level of amorphicity. The absence of the characteristic diffraction peaks of GO indicates an exfoliation of GO within the amorphous structure of the inorganic phase. More interestingly, no diffractions of metallic Ag, Ag_2O , or AgCl suggest that the nanoparticles did not aggregate to bigger silver crystals, got oxidized, or reacted with the chlorine atoms of the initial ZrCl₄ solution during the precipitation.



Fig. 5.67 X-ray diffraction patterns for the initial samples

The nitrogen adsorption isotherms (Fig. 5.68), the pore size distributions (Fig. 5.69), and the parameters of porous structure calculated from the isotherms (Table 5.6) showed that all samples have both micro- and mesoporous structure.



Fig. 5.68 Nitrogen adsorption isotherms for all the samples



Fig. 5.69 Pore size distribution for all samples

Sample	S_{BET} $(m^2 q^{-1})$	$V_{Total} (cm^3 g^{-1})$	$V_{mic} (cm^3 g^{-1})$	$V_{meso} (cm^3 g^{-1})$	V _{mes} /V _T
	(mg)				
ZrOH	208	0.124	0.058	0.066	0.53
AgZrOH	235	0.139	0.061	0.078	0.56
ZrGO	269	0.162	0.068	0.094	0.58
AgZrGO	247	0.156	0.061	0.095	0.61

Table 5.6 Parameters of porous structure calculated from the N₂ isotherms

ZrOH has the highest ratio of the micropores volume to the total pore volume, while AgZrGO has the lowest. For all composites, the surface area and total pore volume increased compared to ZrOH. The highest values of the porous structure parameters were found for ZrGO. The addition of only AgNPs increased the surface area and pore volume by 13% and 12%, respectively. The comparison of ZrGO and AgZrGO showed that AgNPs addition in this case led to an 8% lower surface area, but almost to no change in the pore volume (-2%). The addition of AgNPs led to a broadening of the hysteresis loop (Type H2(b)) between the adsorption and desorption isotherms for AgZrOH and AgZrGO, compared to ZrOH and ZrGO. This suggests a more complex pore structure [12].

As discussed in the previous Sect. 5.1, the SEM images of ZrOH and ZrGO revealed heterogeneous and amorphous surface morphology. The addition of 5% GO led to an enhanced dispersion of the inorganic phase around GO. No structural or morphological differences between the particles were seen at the SEM images of the composites with AgNPs (Fig. 5.70). However, aggregates of NPs were



Fig. 5.70 SEM images of AgZrOH and AgZrGO

observed. These aggregates are dispersed on the outer surface of the particles. They have sizes between 100 and 300 nm and consist of bundles of nanorods.

To identify the chemical nature of these nanoparticles, the dispersion of elements on the surface was analyzed in EDX maps (Fig. 5.71). The results indicated that the NPs consist of exclusively Ag, since the oxygen intensity is dramatically lower at the spots where Ag detected compared to the spots where no Ag detected, and chloride was not detected.

5.2.2.3 Surface Chemistry Analysis

Since in the previous Sect. 5.1 it was revealed that the amount of terminal hydroxyl groups plays a crucial role in the adsorption performance, the amounts of surface functional groups for AgZrOH and AgZrGO were determined using the potentiometric titration method. The results collected in Fig. 5.72 A revealed that the addition of GO led to an increase in the total number of acidic groups, especially the terminal hydroxyl groups. That number for AgZrOH increases by 41% compared to



Fig. 5.71 EDX maps of AgZrGO



Fig. 5.72 Amounts of bridging and terminal groups detected using the potentiometric titration experiments (a) and the density of the terminal groups per unit surface area (b)

that ZrOH. On the contrary, AgZrGO has a slightly lower amount of terminal hydroxyl groups compared to those of ZrGO (-3%). The addition of AgNPs led to a significant increase in the number of bridging groups and thus in the total number of surface functional groups.

Since the weight gain showed a strong dependence on the amount of terminal groups and on the surface area, the densities of the terminal groups per surface area (d_{tgsa}) were calculated and are shown in Fig. 5.72b. Even though both AgNPs and GO addition caused an increase in d_{tgsa} , as a result of the composite formation synergistic effect, the effect was greater for GO. AgZrGO showed the highest d_{tgsa} among all materials studied. The calculated d_{tgsa} are 1.91, 2.39, 3.57, and 3.77 mol m², for ZrOH, AgZrOH, ZrGO, and AgZrGO, respectively.

The differential thermal gravimetric (DTG) curves for the initial samples are shown in Fig. 5.73. For all samples, a gradual weight loss from a low temperature up to 350 °C is observed. The weight loss until 125 °C is assigned to the removal of water (coordinated as ligand or physically adsorbed). Above this temperature, the dehydroxylation of zirconium hydroxide to zirconium oxide takes place. The decomposition of the epoxy groups of GO is barely observable between 190 and 210 °C for the samples with GO [16, 54, 73].

The thermal transformation of $Zr(OH)_4$ to ZrO_2 should lead to a 22.6% weight loss. In our case, the weight loss for all samples was between 13.5 and 16.6% up to 450 °C (Table 5.7). Based on this, we can assume that our materials have an amorphous structure of hydrate zirconium (hydr)oxide.

5.2.2.4 Optical Features—Plasmon Effect

Zirconium hydroxide is photoluminescent under ultraviolet irradiation, emitting blue light. It was reported that its photoluminescence spectrum (PL) can be quenched in different chemical environments, as, for example, a red shift was reported by the replacement of hydroxyl groups [83]. In order to determine whether



Table 5.7 Weight lost % at125 and 450 °C

	Weight loss until	
Sample	125 °C	450 °C
ZrOH	2.3	16.7
AgZrOH	3.4	16.4
ZrGO	6.6	21.6
AgZrGO	6.1	20.8

the presence of AgNPs in the structure of the composites chemically alters the hydroxyl groups as a result of the plasmon effect, the normalized PL spectra of the materials were analyzed (Fig. 5.74).

Pure ZrOH showed a maximum at 510 nm (2.43 eV). This cyan-green emission peak is in a good agreement with the measured band gap for zirconium hydroxide as reported by Whitten and co-workers [83]. They related this emission to the valence-to-conduction band excitation [83]. The addition of the AgNPs led to a broadening of the PL spectrum and to a strong shift to longer wavelengths. For AgZrOH, the maximum of the PL spectrum red-shifted to 555 nm (2.23 eV). This shift was more pronounced for AgZrGO, which showed a maximum at 570 nm (2.17 eV). These changes can be linked to the possible excitation of electrons from the valence band to the hydroxyl ³ Π excited state. In the case of the composites with AgNPs, this decrease of eV indicates alterations in the chemical environment of the hydroxyl groups.

5.2.2.5 Role of the Textural Parameters and Surface Chemistry on the Adsorption

All studied samples were evaluated as adsorbents of 2-chloroethyl ethyl sulfide vapors. The measured weight gains after 24 h of exposure are collected in Fig. 5.75. The addition of the AgNPs resulted in an increased weight uptake. AgZrOH showed a 31% higher weight uptake (122 mg g⁻¹) compared to that on ZrOH (93 mg g⁻¹). The weight uptake on AgZrGO increased 83% compared to that of ZrOH and 10% compared to that of ZrGO (155 mg g⁻¹).

The dependence of the weight gains after 24 h of CEES exposure on the surface area and on the number of terminal hydroxyl groups was analyzed, and rather, low correlation was found with R^2 0.72 and 0.92, respectively. No correlation of the weight gains



Fig. 5.74 Photoluminescent spectra of the studied samples



Fig. 5.75 Weight uptake of ZrOH, AgZrOH, ZrGO, and AgZrGO after 24 h of exposure to CEES vapors

on the amount of the bridging groups or on the micropore volume was detected. On the contrary, the dependence of the weight gain on the density of the terminal groups per surface area and the mesoporous volume showed linear trends with R^2 0.99 and 0.97, respectively. (Fig. 5.76). These correlations suggest that these features play a crucial role in the reactive adsorption process, since the interactions take place in the mesopores.



Fig. 5.76 Dependence of the amount adsorbed on density of the terminal groups and on the mesopores volume for 24 h of CEES exposure

5.2.2.6 Analysis of the Weight Uptake

The progress of the reactive adsorption was studied after various CEES exposure times (Fig. 5.77). ZrOH reached the maximum weight uptake after 36 h (105 mg g⁻¹), while the composites reached after 48 h of exposure. AgZrOH revealed a 73% higher maximum weight gain (161 mg g⁻¹) than did ZrOH, but 21% smaller than did ZrGO (204 mg g⁻¹). The highest weight gain was recorded for AgZrGO (237 mg g⁻¹), which was 125 and 16% higher than those for ZrOH and ZrGO, respectively. The correlations of the maximum weight gain on the density of the terminal groups and the mesopore volume showed linear trends, with R² value 0.95 in both cases.

5.2.2.7 Identification of the Volatile Products in the Headspace

It has been previously shown that the extent of detoxification on the materials can be sufficiently evaluated using two factors: the ability to retain CEES and its degradation products (measured weight increase) and the catalytic degradation extent (monitoring the chromatographs of the headspace) [84]. In the case of ZrOH and ZrGO, the two detected volatile products in the headspace were ethyl vinyl sulfide (EVS) and 1,2-bis(ethylthio) ethane (BETE). The trends in the areas of the peaks representing BETE and EVS in the headspace, measured by GC-MS, with the progress of adsorption are shown in Fig. 5.78. A continuous increase in the amount of EVS was revealed for all samples. The presence of the AgNPs significantly increased the concentration of BETE, as a result of a higher reactivity through the activation of the hydroxyl groups. ZrGO showed almost a twice larger peak area







related to BETE compared to that for ZrOH. The highest concentration of BETE among all the tested materials was revealed also for AgZrGO. Since only EVS and BETE were detected in the headspace, the composites reactively adsorb CEES vapors and convert them to non-toxic products. The addition of AgNPs notably improved the degradation performance.

5.2.2.8 Identification of the Reaction Products Retained on the Surface

The analysis of the reaction products retained on the surface was accomplished by thermal analysis of the exhausted samples and GC-MS analysis of the extracts. Only EVS, BETE, and CEES were detected in the extracts from all samples, even for the samples exposed to CEES for 48 h. For the sake of the comparison with the results described in the previous sub-chapter (5.1), the samples exposed for 24 h were analyzed by TA-MS. The differential thermal gravimetric (DTG) curves for the exhausted samples are shown in Fig. 5.79, while the m/z thermal profiles are collected in Fig. 5.80. The evolution of the m/z signals corresponding to Cl (m/z: 35) and to the saturated diethyl sulfide (m/z: 90) supports the adsorption of CEES. The m/z signal of 88 can be assigned to the unsaturated ethyl vinyl sulfide (m/z: 88, $CH_2=CH_2SCH_2CH_3$), while the m/z 64, 12, and 16 to SO₂, C, and O, respectively.

Compared to the initial samples, the DTG curves for all the exhausted samples revealed four new decomposition features. The first one, at temperature up to 70 °C, is



Fig. 5.79 DTG curves in helium for the exhausted samples



Fig. 5.80 m/z thermal profiles (in helium) of exhausted AgZrGO for the fragments related to fragments of EES (m/z: 90), EVS (m/z: 88), Cl (m/z: 35), $SO_2 (m/z: 64)$, C (m/z: 12), and -OH (m/z: 17)

assigned to the weakly adsorbed CEES and EVS, since the m/z profiles of 35, 88, and 90 showed intense signals in this region. The second one, at 110 °C, can be linked to the removal of EVS, since only m/z of 88 showed peak in this temperature. The third new peak, at 260 °C, can be related to the decomposition of both EVS and CEES, which are strongly retained on the surface by hydrogen bonds. Finally, the last peak at

300 °C can be linked to a further desorption of CEES. The two energetically different sites of the strong adsorption of CEES suggest that the hydrogen bonds between the hydroxyl groups of the inorganic phase and CEES are formed with S or Cl atoms.

5.2.2.9 Conclusions

Amorphous composites of zirconium hydroxide/graphite oxide/silver nanoparticles were successfully synthesized. The addition of AgNPs either to pure zirconium hydroxide or to the composite with GO led to a significant increase of the mesoporosity and the density of the terminal hydroxyl groups. These two factors were found to play the most crucial role in the reactive adsorption process. Interestingly, the existence of AgNPs in the structure resulted in alterations of the chemical environment of the hydroxyl groups due to the introduced plasmon effect. Consequently, the composites with silver nanoparticles showed an improved catalytic degradation. The composite with both GO and AgNPs showed the largest weight uptake and most advanced catalytic degradation yield of CEES to EVS and BETE.

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Chapter 6 Path Towards Future Research

In this chapter results reported in Refs. [1-6] are summarized.

6.1 Oxidized Graphitic Carbon Nitride Nanospheres as a New Composite Component

6.1.1 Graphitic Carbon Nitride

Graphitic carbon nitride(g-C₃N₄) is ametal-free photoactive material which has recently gained attentionof researchers. It has a layered structure, similar to graphite. Themain difference compared to graphite is that its six-member aromaticrings consist of C–N bonds, with both atoms havingsp² hybridization. Owing to its band gapin visible light range and thermal and chemical stability, variousapplications of g-C₃N₄were investigated. In 2009, Wang et al. were the first who reported the photocatalytic ability of g-C₃N₄ to form H₂ in water splitting under visible light irradiation [7–9]. Afterward, many reports followed and they focused on various applications, where the photocatalytic ability of g-C₃N₄ could play a beneficial role.

The main drawback that limits the use of $g-C_3N_4$ as a photocatalyst is the rapid recombination of the formed electron-hole pairs upon the light irradiation [7]. Moreover, the absence of the chemical groups does not provide the opportunity to create bonds with other phases, such as metal oxides, MOF, or nanoparticles. As a result, in many attempts of the application of $g-C_3N_4$ as a composite components rather hybrid materials than composites were formed [2, 10]. To overcome these drawbacks, various studies have focused on the improvement of the photocatalytic performance either via chemical and physical modifications or via the incorporation of graphene, metals, metal oxides/hydroxides, polymers, or nanoparticles [1, 9, 11–17]. The main targets are to delay the electron–hole pair recombination, to alter the band gap, and to increase the conductivity.

6.1.2 Oxidized Graphitic Carbon Nitride Nanospheres

Among all the reported modification methods, the application of the well-known Hummers method of graphite oxidation [18] to graphitic carbon nitride, led to the formation of oxidized graphitic carbon nitride nanospheres, referred to as gCNox [1]. These nanospheres had sizes between 5 and 50 nm (Fig. 6.1). A thermal analysis combined with mass spectrometry showed that they contained a marked amount of chemically unmodified graphitic carbon nitride sheets. These sheets were encapsulated inside the nanospheres (Fig. 6.1d). HRTEM images and XRD results showed an interlayer distance of 0.32 nm, which were in good agreement with the



Fig. 6.1 SEM (a, b), TEM (c), and HRTEM (d) of graphitic carbon nitride nanospheres

literature results [16, 19, 20]. While the unmodified $g-C_3N_4$ powder has a bright yellow color, gCNox powder was white with a limited yellow shade. The color change after oxidation was linked to the widening of the band gap from 2.85 eV for the initial $g-C_3N_4$ [1] to 3.39 eV for gCNox.

Another consequence of the $g-C_3N_4$ oxidation is an increased surface heterogeneity. Even though an XPS analysis revealed the presence of various functional groups on the surface of the nanospheres, the ratio of C to N was found to be the same as that for initial g-C₃N₄ (\sim 0.7). Carboxyl, hydroxyl, secondary amines, and nitroso groups were detected on the surface. These groups increased the surface polarity of the layers and could be the driving force for the formation of the nanospheres. These oxygen-containing functional groups could promote the formation of various composites by participating in the chemical bonds between the gCNox nanospheres and other phases such as metal oxides, MOF, or nanoparticles. They could also act as nucleation centers for the synthesis/deposition of metal oxides/hydroxides. Potentiometric titration results showed that the surface of gCNox was strongly acidic. Oxidation caused the breakage of some C-N bonds in the cyamelurine skeleton of the melem units. This resulted in the rotations of some bonds and in a change in hybridization which, besides polarity, contributed to the formation of shallow bowl-shaped sheets forming the nanospheres. The proposed structure of the nanospheres, taking into consideration all the above, is presented in Fig. 6.2.

As a result of the oxidation applied, the surface dramatically increased from $14 \text{ m}^2/\text{g}$ for g-C₃N₄ to $74 \text{ m}^2/\text{g}$ for gCNox. Interestingly, gCNox was found to be exclusively mesoporous, with the size of the pores between 5 and 50 nm [1]. The size of pores as that of the nanospheres suggests that incorporated gCNox units are responsible for this new morphology. The total pore volume increased from 0.073 cm³/g for g-C₃N₄ to 0.488 cm³/g for gCNox. The enhancement of the porous structure is beneficial for adsorption applications.



Fig. 6.2 Proposed structure of gCNox nanospheres

6.1.3 Graphitic Carbon Nitride Nanospheres as CEES Detoxification Media

The performance of $g-C_3N_4$ and gCNox is reactive adsorbents of vapors of the mustard gas surrogate, CEES, was evaluated at light and in the dark. The weight uptakes after 24 h of vapor exposure under visible light irradiation (WU_{24h}) were 95 and 35 mg/g for gCNox and g- C_3N_4 , respectively. It is worth to mention that $WU_{24h:L}$ of the nanospheres is significantly higher compared to various metal oxides/ hydroxides that were tested at the same conditions [21, 22]. In order to evaluate whether or not light promotes the reactive adsorption/catalysis, the adsorption tests were also performed in the dark. The weight uptakes at these conditions were 58 and 22 mg/g for gCNox and g- C_3N_4 , respectively. The much better performance at visible light than that in the dark indicates the photoactivity of both materials. This was further supported by the analysis of the formed products detected in the headspace of the closed adsorption system or in acetonitrile extracts. For both samples, the only detected product, except unreacted CEES, was ethyl vinyl sulfide (EVS). More EVS was detected when gCNox was used at visible light than in the dark. Thus, light plays a catalytic role promoting the formation of the intermediate transient cyclic sulfonium cation via an intermolecular cyclization pathway. The formed sulfonium cation undergoes a bimolecular elimination reaction followed by the removal of a labile hydrogen, which leads to the formation of EVS.

In order to determine the maximum weight uptakes, the duration of the adsorption tests was extended up to 7 days. The obtained weight uptakes are compared in Fig. 6.3. The maximum weight uptake (WU_{max}) for gCNox (374 mg/g) was three times higher than that for g-C₃N₄ (122 mg/g) [1]. Moreover, on gCNox, the adsorption increased





continuously up to 7 days while on $g-C_3N_4$ the maximum uptake was reached after 3 days. The good performance after oxidation was linked to the nanosized shape of the particles, surface chemistry heterogeneity, and improved porosity.

6.1.4 MOFGCNox Composites as Detoxification Media

The combination of various metal oxides/hydroxides or metal-organic frameworks (MOFs) with graphite or graphite oxide led to composites with significantly improved adsorption performances, predominately due to the synergistic effect [10, 23–31]. Following this research path, limited studies also focused on the application of graphitic carbon nitride as an additive for the formation of hybrids or composites, in order to enrich the solar light harvesting by increasing photoactivity [10, 32]. The first usage of oxidized graphitic carbon nitride nanospheres (gCNox) as an additive/filler was reported in 2017 [2] in nanocomposites with MOF. In this novel material, copper/benzene triacarboxylic acid MOF (Cu-BTC or HKUST-1) was chosen as the main active phase, and the received composite was referred to as MOFgCNox. For comparison, unmodified g- C_3N_4 was also used, and the received material (referred to as MOFgCN) was found to be rather a hybrid rather than a composite.

The addition of gCNox or gCN did not prevent the formation of MOF, since the X-ray diffractograms of MOFgCNox and MOFgCN showed the same pattern as that of pure Cu-BTC. The SEM images for Cu-BTC and MOFgCN showed typical octahedral crystals. For MOFgCNox, the morphological structure of the octahedral crystals was slightly disturbed and the outer surfaces of crystals were covered with spherical nanoparticles of gCNox. An 3D representation of the structure of MOFgCNox is illustrated in Fig. 6.4.



Fig. 6.4 Schematic illustration of MOFgCNox (the black balls represent the spherical nanoparticles of the oxidized graphitic carbon nitride) The first remarkable feature of MOFgCNox was its porosity. Nitrogen adsorption revealed that besides a large volume of micropores/cages (with maximum of the size at 0.59 and 0.81 nm), characteristic for Cu-BTC, the nanocomposites contained a large volume of mesopores (0.201 cm³/g). On the other hand, MOFgCN did not have mesopores. The comparison of the surface areas supported the composite formation in the case of MOFgCNox. MOFgCN showed 30% smaller surface than that of Cu-BTC, which was expected for the hybrid material. On the other hand, the surface area of MOFgCNox increased 60% compared to that of Cu-BTC.

The optical analysis by diffuse reflectance UV–Vis spectroscopy revealed that the coordination chemistry was altered only in the case of MOFgCNox. This was linked to the ability of the nanospheres to act as "giant" acidic linkers, since the XPS analysis showed a large amount of carboxylic groups on the surface of gCNox. The formation of bonds between the nanospheres and the copper was further supported by photoluminescence spectra. While Cu-BTC did not show any emission, the emission pattern of MOFgCN was the same as that of $g-C_3N_4$. On the contrary, no emission, even that characteristic of gCNox was found for MOFgCNox. It was suggested that the exited electrons from the nanospheres were rapidly delocalized in the MOF structure through the formed bonds. This is a crucial behavior, since the delocalized electrons can have a positive effect on the activation of the reactive Cu centers.

The effects of the gCN and gCNox addition to MOF on the detoxification capability were evaluated by exposing the sample to the vapors of a surrogate of nerve agents, dimethyl chlorophosphate (DMCP). The recorded weight uptakes, expressed as mg weight uptake per gram of sample, are presented in Fig. 6.5. The weight uptake on MOFgCN increased 19% compared to that on pure Cu-BTC, after exposure for 24 h at ambient light. On MOFgCNox that increase was 26%. Taking into account that MOFgCNox had the smallest volume of pores and surface area among all three samples, its highest adsorption capacity was linked to the activation of the reactive adsorption centers. Moreover, the mesoporosity played an important role on promoting



Fig. 6.5 Weight uptakes after exposure to DMCP vapors after 24 h at ambient light and in dark

the diffusion of the vapors inside the porous structure and to the active centers. When the adsorption tests were performed in the dark, the weight uptakes followed the trend in the porosity. Cu-BTC showed the highest weight uptake, followed by MOFgCN. On MOFgCNox in the dark, the weight uptake was 30% lower than that on Cu-BTC.

6.2 Mixed (Hydr)Oxides

Mixed metal oxides are other materials with enhanced catalytic properties. Many mixed metal oxides/hydroxides were found to perform better than their single counterparts in various applications [3, 33, 34]. This was linked to synergistic effects, the formation of surface sites with improved reactivity (due to the different oxidation states, altered coordination chemistry, improved oxygen activation, and/ or more lattice defects), and last but not least, to an improved porosity (high surface area, heterogeneity of pore sizes) [35–37].

Among various metal oxides and hydroxides that were tested as reactive adsorbents of CEES vapors, iron- and zinc-based (hydr)oxides revealed the best detoxification performance [38, 39]. Moreover, they were found to be photoactive in visible light. This photoreactivity played a crucial role in the detoxification performance. It enhanced the degradation rate of the toxic compounds. Non-toxic species were the reaction products and simultaneously the physical and chemical adsorption took place. Mixed ZnO-Fe₂O₃ was found as having a high photocatalytic activity under visible light for the photo-degradation of organic compounds (4-chloro-2-nitro phenol and rhodamine 6G) and for a hydrogen evolution [40]. Many nanostructured mixed oxides of Fe with Zn or Cu, prepared from various processors, were tested against vapors of the mustard gas and nerve gas surrogates [3]. In this sub-chapter, a comparison of the performance of pure zinc and iron (hydr)oxides with a mixed Fe/Zn metal oxide is presented.

Three samples were precipitated from chlorides with a controlled addition rate of NaOH. Zinc hydroxide is herein referred to as ZnOH, ferrihydrite—as FeOH, and mixed (hydr)oxide (2:1 ratio of iron to zinc chlorides used for the synthesis)—as FeZnOH. Based on the EDX mapping, the formula of the received mixed (hydr) oxide was ZnFe₃O₅OH and iron and zinc were homogenously distributed in the sample (Fig. 6.6) [3]. The X-ray diffractogram of FeZnOH showed a low level of crystallinity and only two narrow and of low intensity peaks characteristic to two-line ferrihydrite were revealed. No diffraction peaks of ZnO or Zn(OH)₂ were detected. The results of XRD and SEM analysis indicated that in FeZnOH small nanoparticles were attached to the outer bulky particles of mixed (hydr)oxide, which were the aggregates of small nanoparticles of ferrihydrite, as seen on TEM images (Fig. 6.6) [3].

One of the most important features of the reactive adsorbents is their porosity. The measured surface areas and pore volumes for single and mixed (hydr)oxides are collected in Fig. 6.7. The surface area of the mixed (hydr)oxide was very high for this kind of materials and reached 285 m²/g. It was much higher than the surface



Fig. 6.6 SEM (a, b), TEM (c), and EDX mapping (d) images of FeZnOH (Reprinted from Ref. 161, Copyright 2017, with permission from Elsevier)



Fig. 6.7 Parameters of the porous structure calculated from the nitrogen adsorption isotherms

area of ZnOH or FeOH. Based on the composition of FeZnOH, the hypothetical surface area expected for the physical mixture would be 167 m²/g. This value is 41% smaller than the one measured experimentally. It is important to mention that ZnO prepared by the precipitation from its chloride with a controlled addition rate of NaOH had even smaller surface area than ZnOH (15 m²/g) [38].

While ZnOH was a mesoporous material, FeOH had both meso- and microporous structure, with a ratio of meso- to total pore volume of 0.72. Interestingly, even though FeZnOH had both micro and mesopores, its total pore volume was smaller than those in FeOH and ZnOH. On the other hand, it had a marked contribution of micropores.



The main pore size was in the range from 2 to 7 nm. Both meso- and micropores could play important roles in the expected photoreactivity. The former was expected to promote the diffusion of the vapors to the large micropores and to the active centers. The small micropores would be essential for the adsorption of the small molecules formed as a result of the surrogate degradation.

The band gaps were estimated from the Tauc plots. While for ZnOH and FeOH, they were 3.2 and 1.7 eV, respectively, the band gap of mixed (hydr)oxide was 2.2 eV. This suggested the photoactivity of FeZnOH in visible light.

The detoxification/adsorption capability of the mixed (hydr)oxide sample against vapors of the mustard gas surrogate, CEES, was evaluated in the vials-in-vial adsorption system at ambient light. The recorded weight uptakes after 24 h of exposure (WU_{24hL}), expressed in mg per g of the sample, are collected in Fig. 6.8. The performance of FeZnOH was much better than those of single hydroxides. It adsorbed 125 mg/g of the surrogates/its decomposition products. It is important to mention here that the weight uptake on FeZnOH was the highest measured value among various materials that were tested as CEES reactive adsorbents at ambient light for 24 h.

That marked weight uptake on the mixed (hydr)oxide was due to the strong adsorption of CEES and/or its decomposition products. Another important aspect for the detoxification performance, besides adsorption, is the ability of the material to act as a photocatalyst, and to decompose the toxic compounds to less or non-toxic molecules. In the case of FeZnOH, the analysis of the headspace of the closed adsorption system by GC-MS revealed the presence of ethyl vinyl sulfide (EVS), divinyl sulfide (DVS), and 1,2-bis(ethylthio)ethane (BETE). All of them are markedly less toxic than is CEES. The formation of EVS was explained by the dehydrohalogenation that occurs through the formation of an intermediate transient cyclic sulfonium cation, as it was described in details in Chap. 5. The comparison of the performance of FeZnOH to that of mixed (hydr)oxides of Fe and Cu showed that the presence of Zn improves surface reactivity [3].

The detection of DVS and BETE implied that radicals were formed as a result of the photoactivity of FeZnOH. The comparison of the BETE and DVS concentrations in the headspace after 5 days of exposure supported that mechanism. While

concentration of BETE decreased, the concentration of DVS increased. This trend indicated that the material acted continuously as a photocatalyst, degrading BETE, with more DVS formed.

6.3 Reactive and Smart Textiles

The use of the active materials against vapors of CWAs inside the canister of the gas masks was, is, and will be extraordinarily important, since the inhalation of toxic compounds is the fastest way of poisoning. Although various highly toxic compounds, such as blister agents, are deadly harmful even upon contact with the skin. The deployment of mustard gas during WWI resulted in burns all over soldiers' bodies, due to the penetration of vapors through the casual army uniforms. This is the reason why a development of multifunctional protective garments capable to prevent the penetration of CWAs, by adsorption or catalytic detoxification, became an urgent need.

The incorporation of active phases to textiles is one of the most feasible and effective strategies for the design and development of multifunctional/multilayered garments that will provide a sufficient protection level. In the last decades, the research community, academic, military, and industrial, has focused its efforts on cotton or synthetic fibers as a support for the deposition of active phases. These fibrous supports have the advantages of being physically and chemically stable, hydrophilic, breathable, washable, elastic, and easy to be produced in a large scale with a low cost. Cotton fabrics with deposited ferrihydrite nanoparticles or nanostructured composite of MOF (Cu-BTC) with graphitic carbon nitride nanospheres showed a high level of multifunctionality [5, 6]. It was demonstrated that those materials can simultaneous adsorb, degrade, and sense vapors of CWAs.

Another category of fabrics which has been explored as a support for the active phases is the carbon fibers/textiles. They were demonstrated to provide sufficient detoxification activity due to the high porosity and high surface chemistry heterogeneity, especial after chemical activation [4]. Deposition of active inorganic phases can further improve their detoxification activity [41].

In this chapter, we will discuss the detoxification capability of carbon textiles and the importance of their chemical modifications. The latest example of the deposition of active phases on cotton textiles will be also presented. The uniqueness of the herein discussed studies is that the target surrogate was used as vapors, which is the CWA phase that would be used in real life, oppose to surrogates' solutions in various solvent.

6.3.1 Porous Carbon Fabrics

The carbon textiles used in this study were Stedcarb[®] carbon from Stedfast Inc. It is an example of the next generation elastic and porous carbon fabrics [4]. It was



Fig. 6.9 Pictures and thickness of the as-received carbon textiles (CC), after the removal of the polymeric layers (CCm), and after oxidation of CC (CCox) "Adapted with permission from [4] Copyright 2017 American Chemical Society."

received from the US Army Natick Soldier Research, Development & Engineering Center. The as-received sample is referred to as CC. This cloth consists of a main carbon fibers layer that is covered by two polymeric/nylon layers. Since the main purpose was to analyze the properties and the detoxification ability of the main carbon phase, the nylon layers were mechanically removed by immersing CC in boiling water for 30 min. The obtained carbon part, after the removal of the nylon layers, did not lost its elasticity and strength. It is referred to as CCm. To increase the surface chemistry heterogeneity and hydrophilicity, CC was oxidized in a mixture of concentrated nitric and sulfuric acid (25/75 v/v) for 1 day at ambient conditions. Afterward, the modified textile was washed in a Soxhlet apparatus and finally dried at 100 °C for 24 h. The final oxidized textile is referred to as CCox. Pictures of CC, CCm, and CCox can be seen in Fig. 6.9, where also their thickness is reported.

The most crucial feature of the carbon materials for their adsorption applications is their porosity. CCm was found to be microporous, with a bimodal pore size distribution with two maxima at 0.65 and 1.63 nm. The total pore volume was 0.45 cm³/g and the surface area $-922 \text{ m}^2/\text{g}$. Oxidation led to a marked alteration in the porosity. The total pore volume decreased by 58% and the surface area by 63%. The material still had the bimodal pore size distribution but the maxima were slightly shifted to 0.59 and 1.34 nm. The negative effect on the porosity was linked to the pore blockage due to chemical alterations in the carbon matrix and the formation of -O- and/or -N-containing surface functional groups, as confirmed by XPS analysis.

Potentiometric titration results showed a chemically heterogeneous surface with a large amount of acidic functional groups (0.4 mmol/g for CCm and 3.6 mmol/g for CCox). The nature of these surface functional groups was verified by XPS analysis. The formed after oxidation surface groups were predominantly those containing C = O bonds (carbonyl, quinone). The amount of oxygen increased from 13.5 at. % for CCm to 20.4 at. % for CCox. The nitrogen-containing groups of CCm (pyridine, pyrrole, pyridine, amide, amine) were oxidized to pyridine-N-oxide, $C - N^+O - C$, and -NO_x. These groups bring positively charged surface sites that can be involved in a reactive adsorption process [42, 43]. Small amount of sulfur in sulfonic groups was also detected on the surface of both textiles $(\sim 0.5\%)$, which likely originated from the carbon phase itself. H₂SO₄ used for the oxidation could be responsible for a slightly higher amount of S on the surface of CCox compared to that on CCm.

Another important finding was that only CCox showed the ability to form hydroxyl radicals under ambient light irradiation. This feature can play a key role during the interactions of the fabrics with vapors by increasing the surface reactivity and thus the detoxification performance.

In order to evaluate the detoxification capability of the carbon textiles, it is important to take into consideration the following features of the materials: (1) the ability to decompose/convert the vapors to non-toxic products and (2) the ability to adsorb vapors of the mustard gas surrogate, chloroethyl ethyl sulfide (CEES, $C_2H_5SC_2H_4Cl$). Concerning the first feature, CCm revealed only 11% conversion of CEES (the used mass of the surrogate was the 10% of the fabric mass). On the contrary, CCox showed a significantly higher conversion (81%) [4]. The latter is a strong evidence that the oxidation played a catalytic role in increasing the reactivity.

The ability of the textiles to adsorb/retain the vapors of CEES was determined based on the results from the vials-in-vial adsorption tests. The performance at ambient light was expressed as weight uptake (WU_{24h}) in mg per gram of the textile. These values were 272 and 292 mg/g for CCm and CCox, respectively. Interestingly, CCox showed higher WU_{24h} than that of CCm, even though CCox had a smaller total pore volume and surface area. This suggests that surface chemistry is more important than are the textural features. When normalized per a surface area, the weight uptake on CCm was 0.30 mg/cm³, and that on CCox was three times higher and reached 0.87 mg/cm³.

The important finding from the study of the interactions of the carbon textiles with CEES vapors was that the oxidized sample was much more photoreactive than was its nonoxidized counterpart. The amounts of the products formed via radical reactions were dramatically higher on CCox than those on CCm. The OH radicals facilitated the breakage of C–S and/or C–C bonds which led to the formation of various fragments (radicals or ions). The recombination of these fragments resulted in the formation of dimers that consist of two sulfur atoms, such as 1,2-Bis (ethylthio)ethane (BETE, C₂H₅SC₂H₄SC₂H₅) and Bis[2-(ethylthio)ethyl] ether (BETEE, C₂H₅SC₂H₄OC₂H₄SC₂H₅). The improved reactivity of CCox was additionally linked to the oxidized nitrogen-containing surface groups (pyridine-N-oxide, C – N⁺O – C, -NO_x).

Summarizing, the studied carbon textiles were found as promising protection media against toxic vapors. Chemical activation, even such simple as oxidation, can further improve the detoxification performance. The latter was improved without a negative effect on the adsorption/retention capability, even though the porosity decreased. Moreover, the oxidized carbon textile was photoactive and this feature was linked to the formation of hydroxyl radicals. The incorporation of the oxygen-containing groups can also play a crucial role in the deposition of various active phases (nanoparticles, metal oxides, MOFs, or quantum carbon dots), since these groups can act as seeds/anchoring sites for the active phase.

6.3.2 Cotton Fabrics with Deposited Ferrihydrite

The most abundant and widely used biopolymeric textiles/fibers are cotton. It is relatively cheap, hydrophilic, washable, breathable, soft, and flexible [44]. Hydroxyl groups of the monomer (cellulose) were found as important for the durable deposition of nanoparticles or various inorganic active phases [5, 45]. Nanoengineered cotton textiles exhibit unique properties like antibacterial, wrinkle resistance, UV blocking, antistatic, and water repellence [46]. But only recently cotton-based textiles with deposited active phases have been studied as media for (photo)catalytic detoxification of CWAs [5, 6]. Arcibar-Orozco et al. presented a good detoxification performance of ferrihydrite (FH) powder against vapors of CEES [47–49]. Following those results that active phase was deposited on cotton textiles. Even though cotton towel and T-shirt fabric were studied, this part focusses on the later 100% cotton material. It is referred to as TS.

The active phase was deposited immersing a cotton swatch in a ferrihydrite aqueous suspension for 18 h followed by drying for 24 h at 60 °C. This procedure (referred to as dip-and-dry process) was repeated until the maximum amount was deposited (after seven cycles). The received homogeneously brownish colored textile was referred to as TS-Fe, and its image is presented in Fig. 6.10. The mass of FH deposited on the textile was 6.9% (4.8% Fe), that corresponded to a loading of 0.84 mg per cm². The surface area of TS-Fe was 17 m²/g, and that of the initial TS was 8 m²/g.

The low-magnification SEM images revealed that the cylindrical yarns of helical consolidated twisted fibers were not damaged after the dip-and-dry cycles. High-magnification SEM images of TS-Fe showed that the surface of the cotton fibers was coated with thin layers of the inorganic phase, as well as with particles of various sizes and shapes (Fig. 6.11a). EDX analysis confirmed the homogeneous dispersion of FH on the fibers (Fig. 6.11b).

After exposure to CEES vapors for 7 days, pure cotton exhibited a negligible weight gain, while pure FH powder adsorbed 0.31 g per gram of iron. Interestingly, the weight uptake on TS-Fe was almost twice more (0.58 g per g of Fe) and only 4.8% of iron deposited on the fibers was responsible for that increase. The



Fig. 6.10 Pictures of the as-received cotton textile (TS) and the one modified with ferrihydrite (TS-Fe)



Fig. 6.11 SEM image (a) and EDX maps (b) of TS-Fe

normalization of the weight uptakes per a unit of a surface area or total pore volume showed the same trend. This enormous enhancement of the capability to adsorb and retain vapors of CEES and/or the formed compounds during the interactions was linked to (1) the high dispersion of the inorganic phase on the cotton fibers, (2) the high accessibility of the active centers, (3) small nanosize particles of the deposited active phase, and (4) the formation of new interfaces.

In order to determine whether or not TS-Fe had a higher reactivity than that the active phase itself, the nature of volatile species in the headspace of the closed vials-in-vial adsorption system was semi-quantitatively determined by GC-MS. Indeed, TS-Fe showed a broader range of volatile compounds formed compared to a pure FH powder of the same mass as that one deposited on the modified cotton textile. Moreover, the detection of chloro-acetaldehyde in a relatively high amount revealed the enhanced oxidative capability of the ferrihydrite deposited on the cotton textile.

The deposition of ferrihydrite on cotton textiles led to multifunctional protection media/cloths, since the modified material showed a marked adsorption and catalytic decomposition/degradation performance.

6.3.3 Smart Textiles

The above-described textile modified with ferrihydrite cotton showed the enhanced detoxification ability, since they proved to adsorb/retain and simultaneously
catalytically decompose the toxic vapors to non-toxic compounds. Nevertheless, another essential property of advanced and multifunctional materials, targeted to be used in real-life application, is their ability to rapidly sense/detect toxic vapors. Impregnation of MOFgCNox on cotton fabrics found to be a simple, effective, and economically feasible procedure leading to textiles with advantageous performance [6]. The best performing sample is referred to as T-MGox. For the sake of comparison, pure Cu-BTC was also impregnated on cotton textile, and the received material is referred to as T-M.

The successful deposition of MOFgCNox and pure Cu-BTC on the cotton fibers was confirmed initially by SEM images (Fig. 6.12a). The active phases (octahedral crystals of various sizes) were attached to the surface of the fibers. In the case of T-MGox, cavities of sizes from 10 to 50 nm on the surface of the crystals were visible (Fig. 6.12b). They represent the mesopores of MOFgCNox. The preservation of the crystals' structure suggested that the impregnation procedure applied did not affect the morphological and structural features of the active phases. EDX maps further supported the homogeneous dispersion, since copper was detected on the

Fig. 6.12 SEM image of T-M (a) and a high magnification SEM image of one representative particle detected on the cotton fiber's surface of T-MGox (b). Red arrows indicate the mesopores and the yellowish particles represent the oxidized graphitic carbon nitride phase



entire surface of the fibers. The amount of copper estimated by thermal analysis was 1.56% of the total mass for T-M and 0.63% for T-MGox.

Even though the amounts of copper on the textiles were not so high, the adsorption capability of these samples was surprisingly high, especially in the case of T-MGox. The maximum weight uptakes (WU_{max}) expressed as grams of the gained weight per gram of copper (Fig. 6.13) were 2.2 and 6.7 for T-M and T-MGox, respectively. WU_{max} for the powdered active phases were 1.1 and 1.7 g per gram of copper for Cu-BTC and MOFgCNox, respectively. The superior adsorption performance of the textiles compared to the bulky powders was linked to the increased number of copper active sites and their accessibility, as a result of the high and homogeneous dispersion of composites on the cotton fibers.

The initial color of T-M was turquoise (Fig. 6.14a). After exposure to vapors, the color started to change almost instantly to yellow. The change of color was gradual, and the entire textile became totally yellowish after 90 min of exposure. Even though the color of the textiles was changed in less than two hours, the textile continued to adsorb and degrade the toxic compounds for up to 96 h. This suggested a multifunctionability of the reactive centers of the active phase, because some specific features/interactions were responsible for the color change and other for the detoxification. Since CWAs can be deployed as aerosols, the direct exposure



Fig. 6.13 Maximum weight uptakes after exposure to DMCP vapors, expressed as grams per gram of copper



Fig. 6.14 Sensing ability of the smart textiles by color changes after exposure to DMCP vapors for various times (a), the color of the textiles after exposure to 4 μ L droplets of DMCP and CEES (b)

of DMCP droplets was also tested. As seen from Fig. 6.14b, the textiles were also capable to detect the liquid toxic compound, which was shown by exhibiting the same color change as that observed for vapors. Another essential feature was that the textiles were found to be selective to the nerve agent surrogate, since when they were exposed to vapors or droplets of the mustard gas surrogate (CEES), no color change was detected.

These results indicate that these advanced materials can be considered as "smart" textiles, since besides an impressive adsorption and detoxification capabilities, they simultaneously act as colorimetric detector that rapidly sense/detect the toxic vapors or droplets. And more importantly, only a limited amount of deposited active phase on the cotton textile can provide a sufficient protection and fast detection.

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